THE THERMAL DEGRADATION *in vacuo* OF AN AMINE-CURED EPOXIDE RESIN

by

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A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Cape Town.

Somerset West
April, 1969.

ACKNOWLEDGEMENTS

The author would like to thank the Council for Scientific and Industrial Research for the opportunity of carrying out this work and wishes to express his sincere thanks to

C.I.B.A.(ARL)Ltd. for the materials with which this work was done,

Mr. W.P. Baker of A.E.I.(Ltd.) for the loan of the dielectric bridge of his design used in this work,

Dr. S.H. Eggers of the National Chemical Research Laboratory of the C.S.I.R. for mass spectra determinations,

Members of staff of the Chemistry Department of the University of Cape Town for their help in the construction of the apparatus, for NMR spectra determinations and for elemental analyses,

Members of staff of the Propulsion Division, N.I.D.R., C.S.I.R. Somerset West for their help in the construction of apparatus and in the preparation of this thesis,

Mr. D.A. Smith of the Cranfield College of Aeronautics for his guidance in the work on dielectrics.

and Professors E.C. Leisegang and A.M. Stephen for their kind guidance and advice during the work on the degradation products.

ORGANISATION OF THESIS

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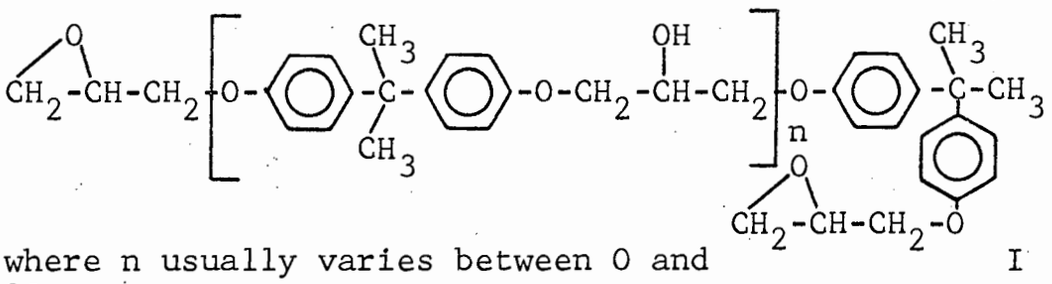
A: Introduction

Epoxide resins belong to the family of organic polymeric materials described as thermosetting. Their properties depend on the reaction of the monomeric resin, which is a material of relatively low molecular weight containing two or more epoxide moieties and which is therefore bi- or poly-functional, (e.g. I) with materials known as hardeners which are polyfunctional, to produce a highly cross-linked structure theoretically of infinite molecular weight. The reaction is known as curing and the final structure is insoluble and infusible by virtue of its molecular weight. The cured resins have good mechanical and electrical properties which make them useful in many fields. Their use in the electrical industry, as adhesives and as surface coatings is now well established.

The structure of the monomeric resins varies. The portion of the molecule to which the reactive epoxide groups are attached can be aliphatic, alicyclic or aromatic and use is made in the surface coatings field of epoxidised novolak resins. The epoxide resins which are produced industrially in the greatest quantities are condensation products of epichlorhydrin and Bisphenol A (2,2-bis-(p-hydroxyphenyl)propane), so named because it is produced by condensing two moles of phenol with one of acetone. These resins have the structure,



where n usually varies between 0 and 20. I

The curing agents fall into three broad categories. The first consists of catalysts, usually Lewis acids, which catalyse the reaction between epoxide groups and hydroxyl groups of the monomeric resins to produce a crosslinked polyether structure. The second consists of either aliphatic, aromatic or polymeric di- or poly-amines or amides. The third consists of aromatic, aliphatic or alicyclic di- or poly-carboxylic acids or, more usually, their anhydrides.

In most of their industrial applications epoxide resins are not subjected to high temperatures. The search, however, for thermostable polymeric materials which has been initiated in particular by the demands of the aerospace industry of the United States for such materials, has led to the examination of the thermal stability of epoxide resins. Very broadly speaking, organic polymers are useful materials in two distinct temperature ranges.[38]

(i) These materials are usually seldom expected to retain their structure and the properties associated with this structure at temperatures above 300°C. Temperatures below 300°C constitute the low temperature region.

(ii) In the field of ablation, however, polymers, in particular thermosetting resins, are subjected to very much higher temperatures. Under these conditions use is made of the degradation of the material to form a char whose insulative properties are valuable. Perhaps the most spectacular example of this use is in the protection by an external layer of ablative material of rocket nose cones from the heat generated by the friction of the air during their return at high speeds from outer space into the earths atmosphere.

The object of this investigation was the study of the low temperature thermal degradation in vacuo of an idealised cured epoxide resin, the condensation product of the diglycidylether of Bisphenol A and p,p'-diaminodiphenylmethane. In particular an attempt was made to study structural changes in the resin network which accompany its degradation.

The thermal stability of epoxide resins, both cured and uncured, has been studied by a wide variety of methods. Investigations have ranged from those designed to give information about the performance of cured epoxides under service conditions to basic studies intended to determine the nature of the molecular processes occurring during degradation.

There is an extensive literature describing investigations whose sole object has been the study of the effect of degradation on macroscopic properties, such as mechanical, electrical and ablative properties. These investigations will not be reviewed as they are not strictly pertinent to this investigation. Bishop and Smith[10] have reviewed the more basic investigations.

In the latter studies epoxide resins of various chemical structures were used. Investigations concerned both pure resins and those cured with many different types of hardener. In most of the investigations commercial resins and hardeners of uncertain composition containing unknown impurities were used. The resins were degraded under various conditions - under vacuum, in air, in inert atmospheres etc. and samples of widely varying geometries, from thin films to those of unspecified and undetermined shape, were employed. Temperatures of degradation ranged from 100°C to 1200°C and both isothermal and heat-pulse methods were used. Methods of monitoring the

degradation included gas-chromatography, infra-red spectral analysis, mass-spectrographic analyses, methods using ^{14}C, differential thermal analysis, differential thermogravimetry and weight loss measurements.[1,2,3,13,20,32,33,35,36,43,44,45,46,47,60] Some investigations concentrated solely on the gaseous products, some on the condensible products, few on all the products and some on none of the products. Few investigations paid any attention to the physical state of the resin during the degradation.

In general, the most useful and informative studies were those in which attempts were made to characterise the relatively low molecular weight compounds which result from the degradation. In this connection investigations using differential thermal analysis, differential thermogravimetry and weight loss measurements, without analytical techniques to back them up, are of limited value. Data such as activation energies which are quoted by workers using these techniques alone are unlikely to be meaningful or instructive.

Mechanisms proposed for the degradation of cured resins, in particular those of Neiman[43,44,45,46] *et al* and Lee,[35,36] often depended on results obtained for the degradation of uncured resins and were, in fact, often extensions of mechanisms proposed for the degradation of the pure resins. It was felt that this needed some critical attention. The work of Stuart and Smith[60] and Keenan[32,33] emphasised the need to consider the cured resin.

There still existed an important consideration, to which hitherto no workers had paid attention. This was the physical state of the resin during degradation

and how degradation subsequently affected the physical state of the resin. This is particularly important when considering results for uncured resins which are liquids or vapours at the temperatures involved, and results for cured resins which are, at least initially, necessarily solids. Correlation of the two sets of data is difficult in view of the widely differing epoxide concentrations involved, but in addition, considerable justification would have to be made for the extrapolation of results for a liquid system to those for a solid system. So far this has not been forthcoming.

In many of the previous investigations relatively high temperatures were used for a variety of reasons. It is axiomatic that the higher the temperature the more complicated is the ensuing reaction.

The aims of this investigation were the following:

1. To obtain a cured resin whose chemical composition and physical state were well characterised.
2. To degrade the resin under specified conditions at as low a temperature as was practicable.
3. To determine what physical changes the resin molecule underwent as a result of purely thermal degradation.
4. To analyse the resin and any products evolved during degradation in order to determine what chemical changes the resin underwent.
5. On the basis of the results, to propose a mechanism for the degradation which would realistically represent the chemical and physical changes occurring during degradation.

Dielectric studies were made to characterise the physical properties of the resin network. These showed conclusively that the network was degraded even at low temperatures, so that mechanisms for the degradation based on the reactions of residual epoxide groups[43] are unrealistic. These results, however, were not susceptible to any quantitative interpretation for reasons discussed later (section F). Analyses of the reaction products were made. Both the major condensible products and the gaseous products of the degradation were identified.

Water, Bisphenol A, phenol, p-isopropylphenol, p-isopropenylphenol, N-methylaniline, N,N-dimethyl-aniline, N-methyl-p-toluidine, N,N-dimethyl-p-toluidine, N,N,N',N'-tetramethyl-p,p'-diaminodiphenyl-methane, 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane, benzofuran, acetaldehyde, carbon monoxide, carbon dioxide, methane, ethane, ethene, chloromethane and nitrogen were identified conclusively and the presence of 2,2-bis-(benzofur-5-yl)propane was suspected. A detailed examination of the structure of the cured resin and its probable modes of decomposition led to the postulation of a reaction mechanism which while tentative in some respects, explained the production of the compounds identified.

The experimental work described in this report is divided into two parts. The first part concerns an investigation of the dielectric properties of the resins before and after degradation.*

*Note: This work was performed by the author under the supervision of Mr. D.A. Smith at the College of Aeronautics, Cranfield, Beds, England, during the period September 1965 to September 1966.

While this work was in progress an attempt was made to analyse degradation products. This preliminary work on degradation products is not reported here since a more detailed and comprehensive analysis of reaction products was subsequently made. This latter is reported in the second part.* A description of the preliminary analyses and their results are given in references 50 and 51.

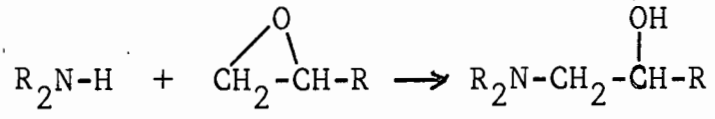
*This work was performed at N.I.D.R. Somerset West, Cape, South Africa, during the period February 1967 to April 1969.

B: Literature Review

B.1: Cure of epoxy compounds with amines

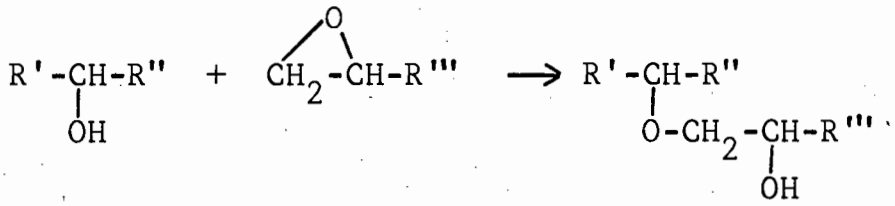
Smith[58] reviewed the literature describing investigations of the reaction between amines and epoxides and Lenz[39] summarised both earlier work and that of Smith. References to the relevant original papers can be found in Smith's paper and Lenz's book.

The overall reaction between an epoxide group and an amino hydrogen is the following:

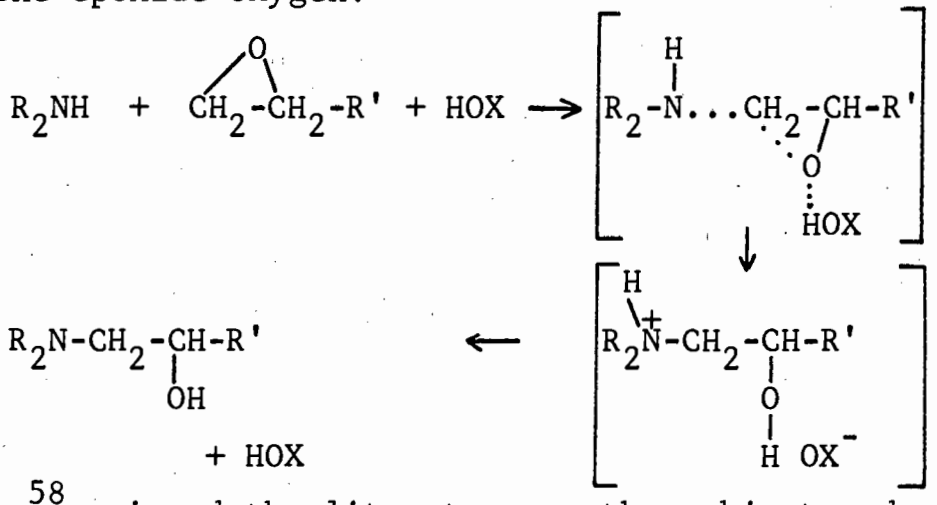


There is much evidence that this simple equation does not represent accurately the mechanism of the process. It appears that the opening of the epoxide ring by an amine is not only catalysed by but requires the presence of a proton donating species for its success. Evidence for this is summarised by Lenz and Smith.

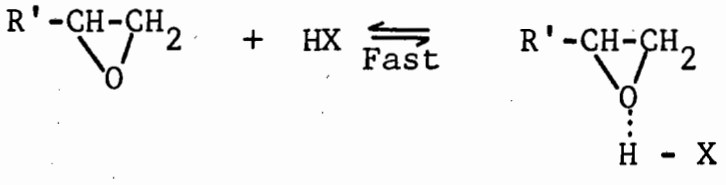
Two papers in particular, are relevant to the mechanism of curing epoxide resins with amines. Schechter, Wynstra and Kurkjy[56] studied the reaction between primary amines and phenylglycidylether, a model compound for epoxide resins. They showed that the reaction of both amino hydrogen atoms with epoxide groups is not accompanied to any appreciable extent by etherification of the aliphatic hydroxyl groups formed in these reactions:

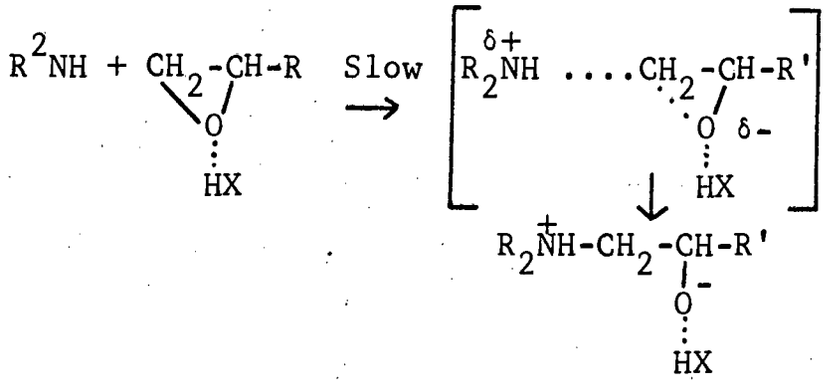


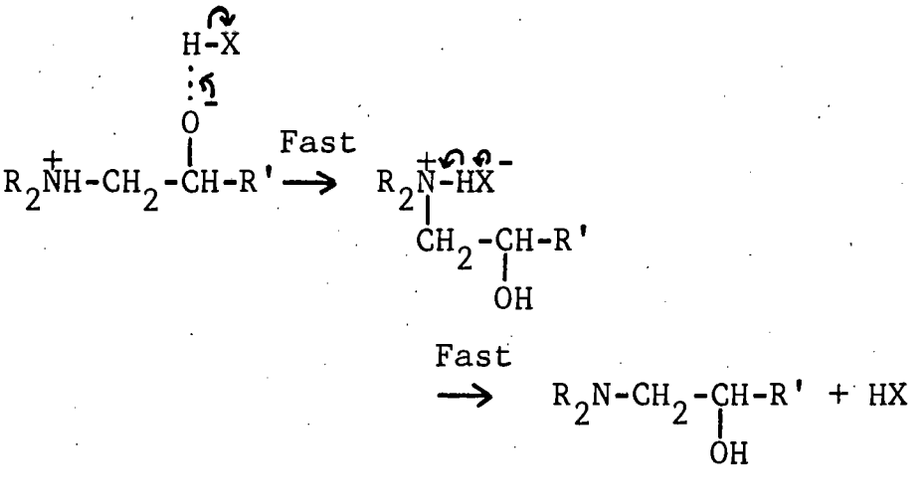
Primary and secondary amines showed no appreciable difference in reactivity towards epoxide groups. The reaction showed a sigmoidal rate curve in the absence of solvents. This was attributed to an autocatalytic effect on the reaction of the hydroxyl groups formed from reacted epoxide groups. In proton donating solvents the reaction was accelerated and the sigmoidal form of the rate curve disappeared. To account for their results the authors proposed the following mechanism in which a proton donating species is involved in the opening of the epoxide group. The essential aspect of the reaction is hydrogen-bonding between this species and the epoxide oxygen:



Smith [58] reviewed the literature on the subject and analysed the kinetics of the reaction. On this basis and from work of his own on the reaction between an epoxide resin and an alkenyl substituted heterocyclic polyamine Smith extended Shechter, Wynstra and Kurkjy's scheme to the following:







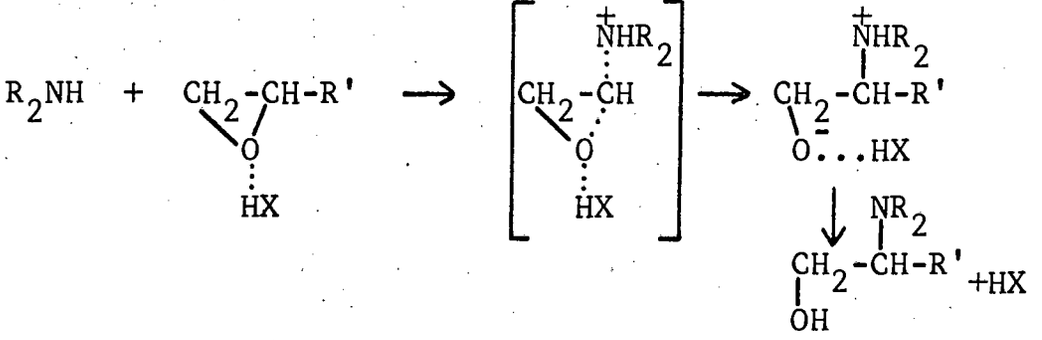
The essential features of the mechanism are:

(1) The initial hydrogen-bonding of the epoxide oxygen with the hydrogen of a proton donating species.

(2) The formation of a termolecular hydrogen-bonded transition state.

(3) That the amino hydrogen involved is not attached to the oxygen involved to form the final hydroxyl group.

The analysis of the available data indicated that the alternative possible ring opening reaction:



did not occur to any appreciable extent.

O'Neill and Cole[47] used infra-red analysis and conventional chemical analyses to study the curing of epoxide resins with fatty acids and amines. Results for amine cures showed the simultaneous disappearance of epoxy groups and amine groups and the appearance of hydroxyl groups. The build-up of non-soluble material was determined by Soxhlet extraction using ethylmethylketone. The main build-up of insoluble material followed the initial most rapid reaction of epoxide groups and was accompanied by little change in epoxide concentration.

Dannenburg and Harp[19] distinguished between degree of conversion of epoxide groups and degree of cross-linking during cure. The essential distinction and inter-relation between these two quantities was demonstrated by measurements on amine-cured epoxide resins. The estimation of epoxide groups was made by infra-red analysis and conventional chemical analysis of swollen samples. The degree of crosslinking was estimated by a specially developed heat indentation test and measurements of equilibrium swelling.

The reaction of epoxy resins and polyamide resins was studied by Peerman, Tolberg and Floyd.[52] Infra-red spectrometry was used to determine the concentration of epoxy groups and mechanical tests on the cured resins were made. The heat distortion temperature proved a sensitive monitor of cure. A discussion of the competing factors of decrease in viscosity at high temperatures and corresponding increased reaction rates during curing was given, leading to the concept of optimum cure temperature.

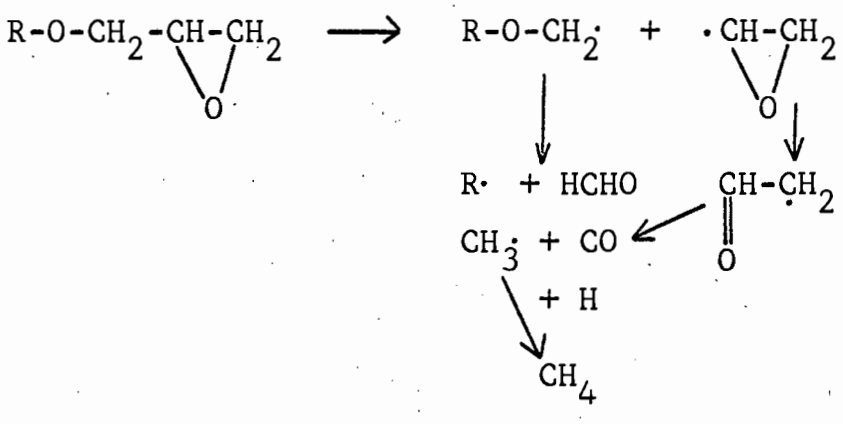
The difficulties inherent in the use of the conventional part of the infra-red spectrum (2-15μ) to study the reaction between amine and epoxy groups (viz. the absorption at approximately the same frequency of hydroxyl and amine groups and the lack of an exact quantitative relation between concentration of epoxy groups and the absorbance at 10.96μ) were circumvented by Dannenburg[18] who used the near infra-red to study the reaction. Dannenburg demonstrated the existence of hydrogen bonding of hydroxyl groups in the liquid which was replaced by a different type of hydrogen bonding upon solidification of the reaction mixture due to cooling or gelling.

A study, using infra-red spectra, of the cure of the diglycidylether of Bisphenol A with p,p'-diaminodiphenylmethane, the resin/hardener system used in this investigation, was performed by the author.[50]

B.2: Degradation of epoxy resins

B.2.a: Thermal degradation

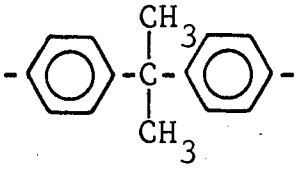
Neiman, Golubenkova, Kovarskaya, Strizhkova, Levantovskaya, Akutin and Moiseev[44] studied the thermal degradation of an uncured epoxide resin at temperatures from 200°C to 500°C. The samples were degraded in previously evacuated tubes and the reaction was followed by observing the pressure rise in the tubes. Chromatographic analysis of the gases produced, which formed some 2% of the products of the reaction, proved the presence of methane and carbon monoxide together with traces of ethane and propane. The condensible products, some 8% of the reaction products, consisted of water and formaldehyde. Infra-red analysis was used to show that appreciable distillation of the low molecular weight fractions in the resin occurred without their modification. An insoluble, infusible mass was left in the reaction tube. A free radical mechanism for the degradation of the resin was proposed to account for the main volatile products:



Water was supposed to have arisen from the polymerisation of the resin to form ether bridges.

Anderson[1,2,3] used the technique of thermo-gravimetry to study the degradation of cured epoxide resins.

Moiseev, Neiman, Kovarskaya, Zenova and Guryanova[43] synthesised an epoxy resin from Bisphenol A with a central ^{14}C atom. The uncured resin was thermally degraded in a sealed, previously evacuated tube at 300°C, 500°C and 800°C. The tubes were cooled and the products which were volatile at room temperature were frozen in traps. Tiny quantities of aldehydes were formed. Carbon monoxide and methane were the main gaseous products. Gases formed a very small proportion of the total products (of the order of one percent at 400°C). The solid residue retained all but a fraction of the original activity. The activity of the carbon monoxide and methane was very low compared with that of the traces of other gases, in particular propane. This was put forward as evidence in support of Neiman et al's[46] mechanism for carbon monoxide and methane formation from epoxy groups. A mechanism was given for the formation of propane and other hydrocarbons. from the unit:



Neiman, Kovarskaya, Golubenkova, Strizhkova, Levantovskaya and Akutin[45] described the degradation of both uncured resin and resin cured with maleic anhydride and polyethylene-polyamine. The reaction was studied by observing the pressure rise due to evolution of gaseous products. Degradation of the cured resins commenced at higher temperatures than those required for the degradation of pure resins. The gaseous products were analysed by gas chromatography; methane, carbon monoxide and propane formed the main products of the degradation of an uncured low molecular weight resin. The same

products were formed during the degradation of the same resin cured with 7% polyethylene-polyamine. Gaseous products only formed 2-5% of the total products. Formaldehyde, acetaldehyde and water were detected and together with the gaseous products formed not more than 15% of the total products. Liquid products, identified as low molecular weight fractions of the resin were found when the pure resin was degraded. The remainder of the products consisted of a hard infusible solid. The non-gaseous products of the degradation of the cured resins were not discussed nor were the cure histories given. The discussion of the degradation and the mechanism proposed followed that in the previous report of these workers.[44] It is not clear whether this discussion was intended to refer to the cured resins or not. Oxidative degradation was briefly mentioned and was supposed to occur via an autocatalytic free-radical reaction involving hydroperoxy radicals.

Lee[35] studied the degradation of epoxide resins, uncured and cured with amine and anhydride hardeners. Commercial resins and hardeners were used and details of cure schedules were given. A variety of techniques was used to study the degradations, including thermogravimetric analysis and differential thermal analysis. Vapour-phase chromatography was used to analyse volatile products of degradation on a hot filament. Mass spectrometry was used to analyse directly the vapours evolved during pyrolysis in a Vycor flask at 350°C or 450°C. The same technique was used to analyse products condensed in a trap during the degradation of resin in a previously evacuated tube heated to 475°C. The results showed that for the

degradation at 350°C of the uncured low molecular weight epoxide resin, the major volatile products were toluene and water. At 450°C the major volatiles were toluene, methylcyclopentadiene and water. The high boiling point products of degradation at 475°C were phenol, cresols, ethyl-substituted phenols, isopropylphenol, isopropenylphenol and Bisphenol A.

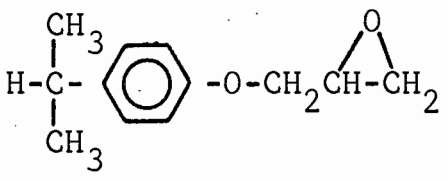
The main volatile product of the degradation at 350°C of a low molecular weight epoxide resin cured with p,p'-diaminodiphenylmethane was water (29.7 mole %). At 450°C the major volatiles were methyl-cyclopentadiene, carbon monoxide, water, carbon dioxide, acetaldehyde, chloromethane and methane. The high boiling point products of degradation at 475°C were similar to those produced in the degradation of the uncured resin. On the basis of these results Lee concluded that the degradation mechanism for the cured resin was similar to that for the uncured resin.

Lee discussed the degradation mechanism proposed by Neiman and workers[43,44,45] and showed that the main course of the degradation could not follow this scheme since the major products were phenolic compounds. Lee proposed several detailed degradation mechanisms to account for the products but all but one start from cleavage of ether groups formed by etherification of epoxide groups. The exception involves isomerisation of the epoxy group to an aldehyde group. These reactions may have occurred during degradation or cure of some of the resins but certainly could not have occurred in the case of an epoxide resin cured with p,p'-diaminodiphenylmethane. Lee makes no reference in his discussion to this system and it is not clear whether his degradation schemes are supposed to apply in this case.

Lee[36] extended his work on the degradation of uncured resins. An epoxy-novolac resin and a Bisphenol A type of epoxide resin were studied. Degradation was performed in tubes heated to 475° under vacuum. Condensible products were trapped and dissolved in acetone. The acetone solution was evaporated and the condensibles separated from water by extraction with dichloromethane. Mass spectrometric measurements showed that phenol and cresols were the main condensible products, with traces of other phenolic species. Lee discussed the results and proposed mechanisms to account for the products based on the formation of Bisphenol A and its subsequent decomposition.

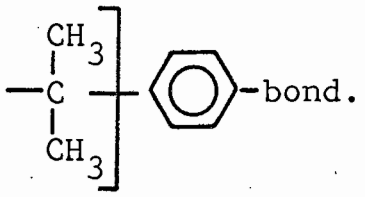
Stuart and Smith[60] pyrolysed a commercial epoxide resin of low molecular weight cured with two different amine hardeners on a hot filament and used gas-chromatography to analyse the products. Analysis was made by comparison of retention times of degradation products with those of single components. In this way, product identification was described as 'highly probable, probable' etc.. Temperatures of degradations were reported as varying from 400°C to 700°C. Hydrogen, carbon dioxide, benzene, toluene, phenol, xylenes and cresols were described as highly probable products; probable products were formaldehyde, acetaldehyde and phenylglycidylether. Both the mechanisms of Neiman et al.[43,44,45] and Lee[35,36] were discussed. It was pointed out that in no work so far had compounds containing nitrogen been reported. Reactions were added to those given by Lee for the mechanism to account for some of the products. Hydrogen was supposed to be lost directly from both

aliphatic and aromatic parts of the cured resin molecule and the formation of phenylglycidylether was proposed. Further reaction of this compound gave phenol, acrolein and benzene. The formation of



was proposed, its subsequent degradation leading to p-isopropylphenol, p-cresol, isopropylbenzene, toluene and xylenes.

Keenan[32,33] used the apparatus of Stuart and Smith to extend their work. The cured resin studied was made from the pure diglycidylether of Bisphenol A and pure p,p'-diaminodiphenylmethane. Keenan analysed the residue left in the pyrolysis head after degradation and products which condensed in an acetone/dry ice trap after passing through the gas chromatograph column. Attempts were made to identify peaks on pyrograms with definite compounds, while thin layer chromatography, followed by analysis by infra-red spectrometry and conventional chemical methods was used in an attempt to characterise the residues and condensible products from the gas chromatograph. Keenan discussed the strength of the chemical bonds in the cured resin and concluded that the two strongest bonds were the aryl carbon-oxygen and aryl carbon-nitrogen bonds. Degradation was thought to be initiated by scission of the weakest bonds viz. the aliphatic carbon-nitrogen bond and the

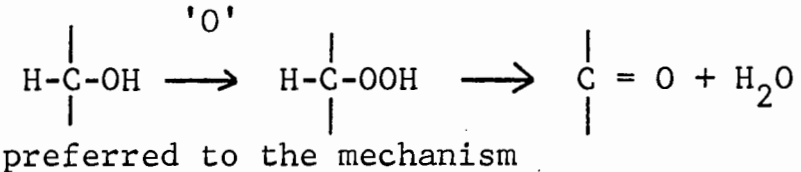


Reactions which could follow these two processes were detailed to account for some of the products reported in this and Lee's work.

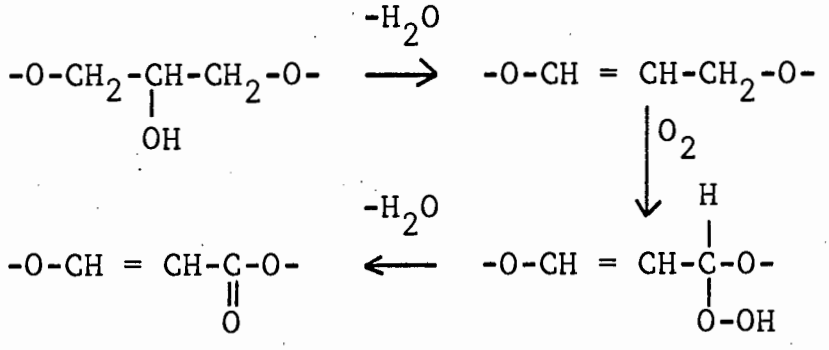
Preliminary work by the author[50,51] on the identification of the reaction products from the degradation of the same resin/hardener system revealed the presence of phenol, N-methylaniline and N,N-dimethylaniline.

B.2.b: Oxidative degradation

Park and Blount[48] studied the oxidation of acid cured epoxide resins at 180°C in the form of thin films. The effects of variables such as air dry time, post-cure treatment, film thickness, molecular weight of resin and solvent formulation on rate of oxygen uptake by the films was reported. Infra-red spectra of oxidised films showed that oxidation was accompanied by a decrease in the concentration of hydroxyl groups together with an increase in the concentrations of carbonyl groups. No evidence of the formation of carbon-carbon double bonds was found, so that the mechanism



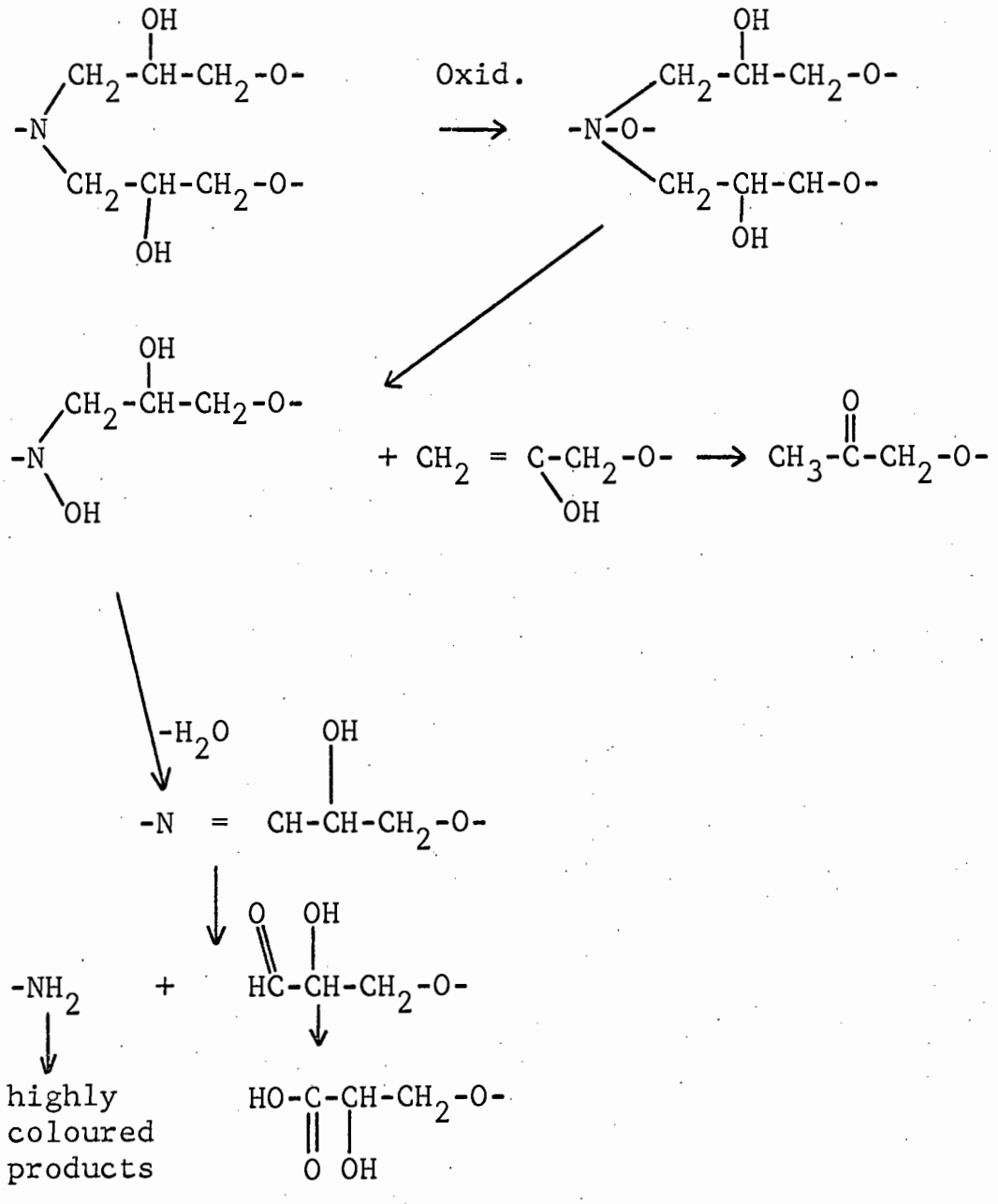
was preferred to the mechanism



but it was realised that the former was by no means a complete description of the process.

Neiman, Kovarskaya, Yazvikova, Sidnev and Akutin[46] studied the oxidation of a low molecular weight epoxide resin hardened with polyethylene-polyamine and maleic anhydride at temperatures in the range 160° - 250°C. The cured resin in the form of a powder was placed in a tube connected to a vacuum apparatus such that an initial pressure of oxygen could be introduced and the subsequent pressure variation observed. At all temperatures and oxygen pressures there was no pressure change for a time followed by a decrease in oxygen pressure. This induction period was shortened by higher oxidation temperatures and by higher oxygen pressures. The reaction was supposed to be autocatalytic and to proceed by a branched free-radical chain mechanism. Hydroperoxides acted as a source of free radical centres. Hydroperoxides were analysed by conventional chemical techniques.

Conley[13] and Dante and Conley[20] reported the results of infra-red analysis of films of cured epoxide resins cast on rock salt windows during oxidation at temperatures around 225°C. Commercial resins were fractionated and individual fractions cured with m-phenylenediamine and diethylenetriamine. The oxidative degradation of a film made from a low molecular weight resin and m-phenylenediamine was accompanied by the growth of peaks at 5.8 and 6.0μ in the infra-red spectrum, as was that of the resin cured with the aliphatic amine. Conley[13] showed that the weak link in the resin is the curing N-C link. On the basis of the behaviour of 1,2-aminoalcohols when oxidised and the results of the investigation a mechanism was proposed for the reaction:


Oxid.
highly
coloured
products

B.3: The infra-red spectra of epoxy resins

The work of O'Neill and Cole,[47] Dannenburg and Harp[19] and Dannenburg[18] was reviewed in section B.1.. The book by Bellamy[6] "Infra-red spectra of complex molecules" provided an invaluable general reference. Lee and Neville's book 'Epoxy Resins'[37] was also consulted in this context.

Patterson[49] published the spectra of twenty-six epoxy compounds. Correlation of the spectra indicated that absorption characteristic of the oxirane ring occurred at about 8μ , 11μ and 12μ . The position of the latter two bands varied somewhat from compound to compound. Epoxy ethers studied also showed absorption at 12.2μ which could have been due to the oxirane ring.

Feazel and Verchot[23] reported the use of potassium bromide discs cemented together with an epoxy-resin/ hardener mixture to study cure.

Henbest, Meakins, Nicholls and Taylor[29] studied the characteristic absorption due to the stretching of carbon-hydrogen bonds in the epoxide ring, which appeared between 3050-2990 cm^{-1}.

Sugita and Ito[61] studied the pyrolysates of cured unfilled epoxide resins. Identification of the hardener used was made possible by this technique. Assignments of peaks in the infra-red to absorptions due to specific groups were made.

Keenan[32,33] whose work was reviewed in section B.2.a., used infra-red spectra extensively. Absorptions in the infra-red spectra of degradation products were discussed in relation to the molecular processes supposed to occur during degradations. Absorptions in the infra-red spectrum of the diglycidyl-ether of Bisphenol A were correlated as far as possible with individual chemical groups in the compound.

B.4: Dielectrics

B.4.a: Recent comprehensive review articles on the general theory of the dielectric properties of matter, (Wyllie[62] and Cole[12]), specifically on the dielectric properties of solids (Meakins[41]) and more specifically on the dielectric properties of polymeric systems (Curtis,[15] Mikhailov and Borisova,[42] Reddish,[54] Baird[5] and Pegoraro[53]) are summarised in sections C.1 and C.2.

The recently published book 'Anelastic and Dielectric Effects in Polymeric Solids' by McCrum, Read and Williams[40] provides a comprehensive review of the theory of dielectric relaxation of polymers and of the dielectric properties of a wide variety of polymeric systems.

B.4.b: Dielectric properties of epoxy resins

Kobale and Löbl[34] studied the dielectric properties of a low molecular weight epoxide resin cured with tetrahydrophthalic anhydride under a variety of cure conditions. A dispersion region (at high frequencies and low temperatures) was associated with the movement of hydroxyl groups and another dispersion region (at low frequencies and high temperatures) was associated with the softening of the resin and with the relaxation of the resin network. A study was made of the effects of cure-time, hardener concentrations, cure temperature and plasticisers on the dielectric properties, and in particular on the second dispersion region. A study was made on the change in dielectric properties during cure of the above resin/hardener system and also of a resin cured with p,p'-diaminodiphenylmethane. The specific resistance of resins cured with different amounts of hardeners was measured as a function of

temperature. Eyring's absolute reaction rate theory was applied to the high temperature loss region. For this region plots of the frequency of loss maxima against the reciprocal of the absolute temperatures gave straight lines and from these plots a study of the effect of hardener concentration on activation enthalpy and activation entropy was made. The results were discussed in the light of the molecular processes occurring during mixing of resin and hardener, and cure.

Dasqupta and Mital[21] studied the dielectric properties in the frequency range 5 c/s to 50 kc/s and the temperature range 12-95°C of a commercial resin, a commercial hardener (phthalic anhydride) and cure mixtures of the two. The high loss exhibited by the pure components at frequencies below 1 kc/s was thought to be due to conduction by ionic impurities.

Haran, Gringras and Katz[28] studied the changes in loss tangent and dielectric constant accompanying the curing of a commercial epoxide resin with diethylene-triamine at constant temperature. The loss tangent/time curves were typically represented by a decrease followed by an increase to a maximum and subsequent decrease. No attempt was made to explain the curves but their possible application to the monitoring of cure was discussed.

Antonov *et al.*[4] examined the properties of a Bisphenol A type resin, both uncured and cured with diethylamine and maleic anhydride. A plot of tan δ for the amine cured resin showed two dispersion regions, as was found in the present investigation. These workers studied the effect of molecular weight on the dielectric properties of the uncured resins and

also the effect of different quantities of curing agents on these properties during cure.

C: Summary of Dielectric Theory*

C.1: General dielectric theory

The theory may conveniently be split up into two parts:

i) that which concerns loss-free materials or lossy materials in a state of equilibrium viz. the theory of dielectric polarisation.

ii) the theory of dielectric relaxation which attempts to describe the absorption of energy by a lossy material subjected to a non-constant field.

C.1.a: Dielectric polarisation

The application of an electric field to a dielectric produces a polarisation of the dielectric i.e. dipoles are set up in the material such that over any large enough region there is a nett separation of charge. On a molecular level polarisation may be due to several processes.

i) Electronic polarisation i.e. the perturbation of electronic orbitals or, roughly speaking, the relative displacement of electrons and atomic nuclei.

ii) Atomic polarisation i.e. the stretching, twisting and bending of chemical bonds.

iii) Orientation polarisation due to the tendency of permanent dipoles of the dielectric to align themselves with the field.

*Note: The rationalised M.K.S. system of units will be used.

In addition to the above three types, interfacial or Maxwell-Wagner type polarisation may occur at the interface of two materials differing in electrical conductivity.

Macroscopically a vector $\bar{D}$, the displacement, may be defined as the charge moved/unit area. Experiments show that for low intensity fields applied to non-lossy isotropic dielectrics $\bar{D}$ is related to the field $\bar{E}$ by the relation

$$\bar{D} = \epsilon\epsilon_o\bar{E}$$

where ϵ_o is a universal constant and ϵ a constant (at a fixed temperature and fixed frequency of the field) which is characteristic of the dielectric.

Any dielectric theory must relate measurable physical quantities to significant molecular quantities calculable, at least in principle, from molecular theories. Charges and current should be put in terms of electrons and nuclei and their motions, macroscopic quantities then being obtained by averages over molecular quantities. By assuming Coulomb's Law for the force between charges and by some purely mathematical manipulation, the displacement $\bar{D}$ may be related to the field $\bar{E}$, the polarisation $\bar{P}$ (i.e. the no. of dipoles/unit volume) and higher multiple moment densities by the relation

$$\bar{D} = \epsilon_o\bar{E} + \bar{P} + \text{higher terms}$$

The elimination of $\bar{D}$ from these two equations forms the basis for most of the equations which attempt to relate the macroscopically accessible ϵ with molecular quantities. The macroscopic field $\bar{E}$

in the equations is not in general equal to the field of external charges. The computation of the local field at a molecule, which is the vector sum of the macroscopic field and fields due to the other molecules present which are violently fluctuating quantities, provides difficulties.

At present, detailed theories exist for gases of simple molecules at low pressures. For more complicated molecules and gases at higher densities, liquids and solids, simplifying assumptions or models, often of dubious validity, have to be used.

C.1.a.i: Polarisation of gases

The static polarisation of dilute gases may be treated by assuming that the molecules are independently polarised by an external field $\bar{E}_o$, thermal collisions only serving to maintain equilibrium between the internal and external motions of the molecules. Because of the independence of the polarisation, the total polarisation is given simply by the sum of the polarisations of individual molecules

$$\bar{P} = N \frac{\langle \bar{m} \rangle}{V}$$

where N is the no. of molecules in volume V and $\langle \bar{m} \rangle$, the average dipole moment of each molecule.

Ignoring any higher terms than the polarisation

$$\bar{D} = \epsilon_o \bar{E}_o + \bar{P}$$

$$\bar{D} = \epsilon \epsilon_o \bar{E}_o$$

whence $(\epsilon - 1) \epsilon_o \bar{E}_o = \bar{P}$

$$= \frac{N}{V} \langle \bar{m} \rangle$$

$\bar{P}$ and $\bar{E}$ are aligned since the gas is isotropic whence

$$(\epsilon-1)\,\epsilon_o|\bar{E}_o| = \frac{N}{V}\langle\bar{m}.\bar{e}_o\rangle$$ where $\bar{e}_o$ is unit vector in the field direction

Debye represented the moment $\bar{m}$ by the sum of an induced moment $\bar{\eta} = \alpha\bar{E}_o$ with α a scalar polarisability and a permanent moment $\bar{\mu}$ directed along some molecular axis.

$$\bar{m} = \alpha\bar{E}_o + \bar{\mu}$$

$$m.e_o = \alpha\bar{E}_o.\bar{e}_o + \bar{\mu}.\bar{e}_o$$

$$= \alpha|\bar{E}_o| + |\bar{\mu}|\cos\theta$$ where θ is the angle between the molecular axis and $\bar{E}_o$

$$\langle\bar{m}.\bar{e}_o\rangle = \langle\alpha|\bar{E}_o| + |\bar{\mu}|\cos\theta\rangle$$

$$= \alpha|\bar{E}_o| + |\bar{\mu}|\langle\cos\theta\rangle$$

$\langle\cos\theta\rangle$ was obtained by considering the energy of a dipole aligned at an angle θ related to the field direction and by using the first term of a Langevin expression for the distribution of orientations with respect to the field:

$$\langle\cos\theta\rangle = \frac{|\bar{\mu}||\bar{E}_o|}{3kT}$$

substituting for $\langle\bar{m}.\bar{e}_o\rangle$ gives

$$(\epsilon-1)\epsilon_o|\bar{E}_o|\frac{V}{N} = \alpha|\bar{E}_o| + \frac{|\bar{\mu}|^2|E_o|}{3kT}$$

whence $$\epsilon-1 = \frac{N}{\epsilon_o V}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

where $\mu = |\bar{\mu}|$

Quantum Mechanical calculations show that representation of $\bar{m}$ by $\bar{m} = \alpha\bar{E}_o + \bar{\mu}$ is approximately justified in most cases.

At moderate gas densities the assumption used in the above derivation that the macroscopic field is indistinguishable from the local field as the field of external charges is no longer valid.

If a gas is introduced between the plates of a parallel-plate condenser such that the charges on the plates remain constant, the macroscopic field between the plates is given by

$$\bar{E} = \frac{\bar{E}_o}{\epsilon} \quad \text{where } \bar{E}_o \text{ is the original field.}$$

Lorentz calculated the local field at a molecule which had polarisability α and was situated on a regularly spaced lattice of cubic symmetry, as

$$\bar{E}_L = \bar{E}\,\frac{(\epsilon+2)}{3}$$

Representing the moment of the molecule as $\alpha\,\bar{E}_L$, and summing over all molecules, substitution into

$$(\epsilon-1)\epsilon_o\bar{E} = \frac{N}{V}\,\alpha\bar{E}_L$$

gives

$$\frac{(\epsilon-1)}{(\epsilon+2)} = \frac{N\alpha}{3\epsilon_o V}$$

Assuming that $\bar{E}_L$ is also the field which might tend to orientate permanent dipoles gives

$$\frac{(\epsilon-1)}{(\epsilon+2)} = \frac{N}{3\epsilon_o V}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

The use for a non-polar gas of a field which is computed for a regularly spaced lattice needs justification. The introduction of the term for permanent moments is even more suspect as the assumptions used by Lorentz in computing the local field are no longer valid. More detailed calculations of the local field show that the function

$\frac{(\epsilon-1)}{(\epsilon+2)} \frac{V}{N}$ is not necessarily simply related to molecular quantities.

In practice the expression

$$\frac{(\epsilon-1)}{(\epsilon+2)} = \frac{N\alpha}{3\epsilon_o V}$$

describes the polarisation of non-polar gases and some non-polar liquids quite well. For polar gases

$$\frac{(\epsilon-1)}{(\epsilon+2)} = \frac{N}{3\epsilon_o V}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

is less good and can be very bad for polar liquids with high dielectric constants. The detailed theories are complicated, however.

C.1.a.ii: <u>The polarisation of liquids</u>

Since the expression

$$\frac{(\epsilon-1)}{(\epsilon+2)} = \frac{N}{3\epsilon_o V}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

does not describe adequately the dielectric constant of polar liquids, a theory for these is needed. Most theories for liquids use variations or modifications of Onsager's model. Onsager represented a polar molecule in a liquid as a point polarisable dipole at the centre of a sphere of exclusion of radius a, having molecular dimensions. The surroundings were taken to be a continuum of dielectric constant surrounding the void. A dipole of moment $\bar{m}$ in the

cavity induces a polarisation of the continuum surrounding the cavity which in turn gives rise to a reaction field in the cavity given by

$$\bar{R} = \frac{2(\epsilon-1)}{(2\epsilon+1)} \frac{\bar{m}}{a^3}$$

Representing $\bar{m}$ by $\mu + \alpha \bar{R}$ gives

$$\bar{m} = \mu \Big/ \left(1 - \frac{2(\epsilon-1)}{(2\epsilon+1)} \frac{\alpha}{a^3} \right)$$

A uniform macroscopic field $\bar{E}$ outside the cavity gives rise to a uniform macroscopic field $\bar{G}$ inside the cavity

$$\bar{G} = \frac{3\epsilon\bar{E}}{2\epsilon+1}$$

The resultant field inside the cavity is $\bar{G} + \bar{R}$, but it is clear that, since $\bar{R}$ lies parallel to $\bar{m}$, only $\bar{G}$ plays any part in orienting the dipole. The sum of mean induced and mean square orientation moments gives

$$\epsilon-1 = \frac{N_o}{\epsilon_o} \frac{u}{V} \left(\frac{3\epsilon}{2\epsilon+1} \right) \left(\frac{\alpha}{\left(1 - \frac{2(\epsilon-1)}{(2\epsilon+1)a^3}\right)} + \frac{\mu^2}{\left(1 - \frac{2(\epsilon-1)}{(2\epsilon+1)} \frac{\alpha}{a^3}\right)} \right)$$

where u is the no. of moles and N_o the no. of molecules per mole.

Onsager assumed that the spherical molecules completely filled the volume they occupied:

$$u\ No\ \frac{4}{3}\pi a^3 . = V$$

This is equivalent to saying that the mean resultant local field at each molecule is the Lorentz field i.e.

$$\langle \bar{R} + \bar{G} \rangle = \frac{(\epsilon+2)\bar{E}}{3}$$

Using this assumption and putting $\mu = 0$ yields the expression:

$$\frac{(\epsilon_\infty - 1)}{(\epsilon_\infty + 2)} = \frac{u\ No}{3\epsilon_o V}\alpha$$

where ϵ_∞ refers to the dielectric constant at frequencies such that orientation polarisation is prohibited. This is the classical expression, using the Lorentz field, for the polarisation of polar gases or liquids. Putting $\mu \neq 0$ and again using the volume assumption leads to the expression

$$\frac{(\epsilon-\epsilon_\infty)(2\epsilon+\epsilon_\infty)}{\epsilon(\epsilon_\infty+2)^2} = \frac{No}{3\epsilon_o}\ \frac{\mu^2}{3kT}\ \frac{u}{V}$$

which is a distinct improvement on the classical expression, using the Lorentz field, for the polarisation of a polar liquid.

Modifications of Onsager's treatment involve changing the shape of the molecular cavity or avoiding the volume assumption. Onsager's expression does not describe with even reasonable accuracy the dielectric constants of hydrogen bonded liquids. Theories have been put forward to describe the properties of these materials.

C.1.a.iii: <u>The polarisation of solids</u>

Crystalline solids may be anisotropic. In this case the quantity ϵ in the relation

$$\bar{D} = \epsilon\epsilon_o\bar{E}$$

is a second rank tensor.

The dielectric properties of solids depend on the type of solid considered. In general, in ionic solids the forces involved in the relative displacements of electron clouds and nuclei are small, giving rise to absorption in the far infra-red, and hence only electronic distortions contribute to the polarisability. At low frequencies, however, alkali halide crystals have dielectric constants of 5 to 30 or more, indicating that ionic displacements contribute to the polarisability.

Molecular crystals of non-polar compounds form the type of idealised system for which the Lorentz field was calculated and, apart from anomalies due to phase transitions, seldom show interesting properties. Molecular crystals of polar molecules show more interesting behaviour. It appears that in the crystal, orientation of the dipoles may be possible. In many polar molecular crystals, abrupt changes in the dielectric constant occur below the melting point and these are usually associated with changes in the rotational freedom of the dipoles which accompany changes or anomalies in other properties such as specific heats, volume, and crystal type.

Computation of dipole interactions is in general a complicated problem. Molecular orientation in solids is often discussed by considering one molecule whose rotational movements are supposed to be hindered by the presence of potential barriers whose form may be suggested by the packing of neighbouring molecules. Treatments of the pair-wise interaction of dipoles, however, show no features which may be represented by temperature dependence on fluctuating potential barriers related to the angular co-ordinates of a single molecule. There may be cases for which the one-molecule model is an adequate description, but it

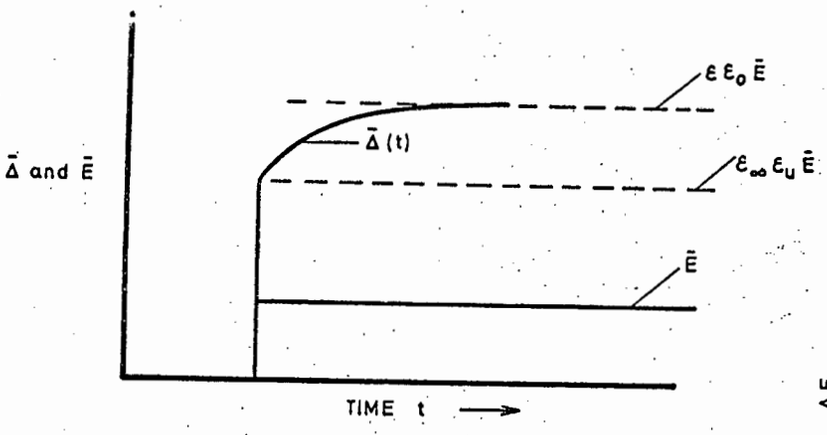


Figure 1

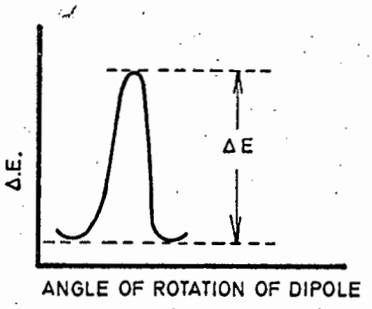


Figure 4

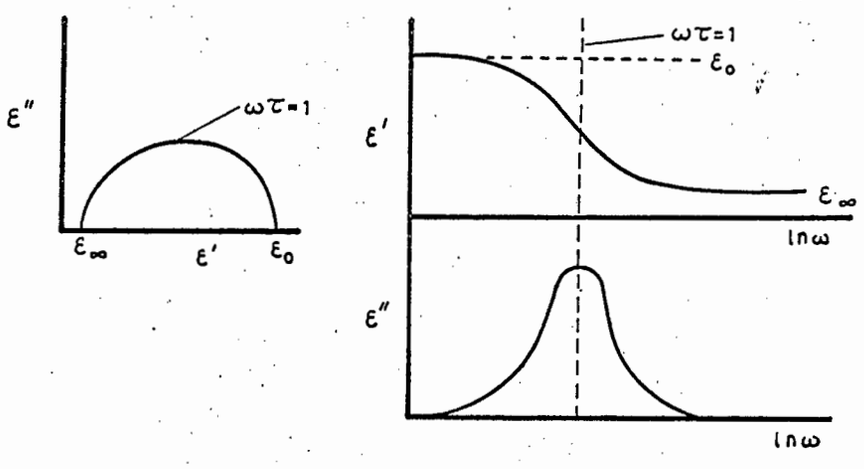


Figure 2

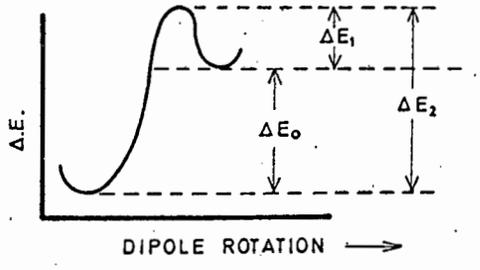
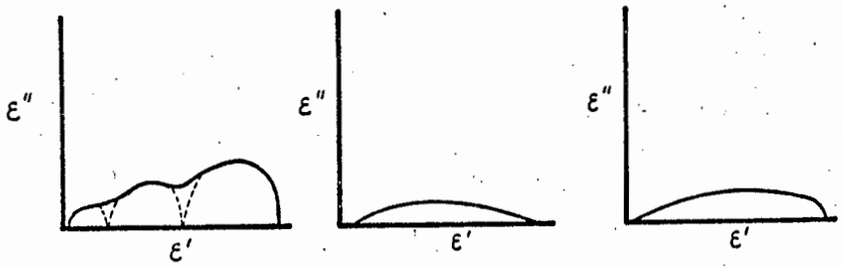


Figure 5



a) MULTIPLE b) CIRCULAR ARC c) SKEWED ARC

Figure 3

is not generally adequate and cannot be applied to any set of data. This is important since this model is often used when discussing relaxation processes.

C.1.b: Relaxation of dielectrics

If a dielectric is submitted to a field which is a step function as shown in figure 1, the displacement often shows the behaviour shown by the curve in figure 1.

A practically instantaneous response of the dielectric is followed by a slower response which asymptotes to an equilibrium value. The rapid initial response is attributed to induced electronic or nuclear displacements and is hence as much a function of intra-molecular structure as molecular interaction. The slower response for times longer than 10^{-12} seconds is usually considered the domain of dielectric relaxation. For these times the steady-state response to a sinusoidal field is more easily studied than transients due to instantaneous changes in the applied field. Both types of response, however, are subject to the same molecular dynamics and, providing that the principle of super-position holds (viz. that the response to separate successive applications of fields is the sum of responses to each separate application of a field), can be related by Laplace or Fourier transform theory. The same theory shows that ϵ' and ϵ'' are not independent functions of frequency or temperature.

Clearly the relation

$$\bar{D} = \epsilon\epsilon_o\bar{E}$$

precludes any time dependent effects and this relation often holds at optical frequencies (where no resonance absorption occurs) at which orientation polarisation

cannot occur because of the high frequencies.

Consider a field which varies with time as

$$E = E_o \cos \omega t$$

If dielectric absorption takes place $\bar{D}$ no longer follows $\bar{E}$ and there is a phase difference δ between them so that $\bar{D}$ can be written

$$\begin{aligned} D &= Do \cos(\omega t - \delta) \\ &= Do(\cos \omega t \cos \delta + \sin \omega t \sin \delta) \end{aligned}$$

i.e. a component Do cos δ is in phase with E and a component Do sin δ is $\frac{\pi}{2}$ radians out of phase with E.

E can be written concisely as

$E^* = Eoe^{i\omega t}$ where E^* denotes a complex quantity with the convention that the intensity of the field is given by the real part of the complex quantity. D^* is then given by

$$D^* = Do\ e^{i(\omega t - \sigma)}$$

Suppose $D^* = \epsilon^* \epsilon_o E^*$

i.e. $$\frac{D^*}{\epsilon_o E} = \epsilon^*$$

Then $$\epsilon^* = \frac{Do\ e^{i(\omega t - \sigma)}}{\epsilon_o E_o\ e^{i\omega t}} = \frac{D_o}{\epsilon_o E_o}\ e^{-i\delta}$$

Expanding gives $$\epsilon^* = \frac{D_o}{\epsilon_o E_o} (\cos \delta - i \sin \delta)$$

so that ϵ^* can be written

$$\epsilon^* = \epsilon' - i\ \epsilon''$$ with

$$\epsilon' = \frac{D_o}{\epsilon_o E_o} \cos \delta$$

and $$\epsilon'' = \frac{D_o}{\epsilon_o E_o} \sin \delta$$

and $$\frac{\epsilon''}{\epsilon'} = \tan \delta$$

Implicit in the assumptions that D^* is related to E^* by

$$D^* = \epsilon_o \epsilon^* E^*$$

is the assumption of linear behaviour.

For a stepwise application of a field the simplest form of relaxation is an exponential rise in $\bar{D}$ after the initial rapid increase in $\bar{D}$. This is Debye's treatment of relaxation and one which is often found experimentally. The complex dielectric constant for a sinusoidal field is given in this case by

$$\epsilon^* = \epsilon_\infty + \frac{(\epsilon o - \epsilon_\infty)}{(1 + i\omega\tau)}$$

where τ is the macroscopic relaxation time, ϵ_o the dielectric constant at frequencies below the absorption and ϵ_∞ at frequencies above.

Separating real and imaginary parts gives

$$\epsilon' = \epsilon_\infty + \frac{\epsilon o - \epsilon_\infty}{1+\omega^2\tau^2}$$

$$\epsilon'' = (\epsilon o - \epsilon_\infty)\frac{\omega\tau}{1+\omega^2\tau^2}$$

This behaviour may be represented by figure 2.

A plot of ϵ'' against ϵ' (Cole-Cole plot in the complex plane) is a semi-circle.

Debye-type relaxation is also described by the 1st order differential equation for the polarisation, P.

$$\tau \frac{dP}{dt} + P(t) = (\epsilon o - \epsilon_\infty)E(t)$$

Many models can give rise to this equation so that the conformation of experimental data to Debye-type relaxation is, of itself, no confirmation of the validity of any one particular model.

Often relaxation processes exhibit a different time dependence than that described by Debye. Some examples of Cole-Cole plots are given in figure 3.

Formally such curves can always be constructed from a linear superposition of relaxation processes of the simplest type (i.e. Debye-type), each with its own characteristic relaxation time τ_i

$$\epsilon^* - \epsilon_\infty = \sum_i \frac{Fi}{1 + i\omega\tau_i} \quad \text{where} \quad \sum F_i = \epsilon_o - \epsilon_\infty$$

More generally for a continuous distribution of relaxation times

$$\epsilon^* - \epsilon_\infty = \int_o^\infty \frac{F(\tau)d\tau}{1+i\omega\tau^2} \quad \text{where} \quad \int_o^\infty F(\tau)d\tau = \epsilon\, o - \epsilon_\infty$$

$F(\tau)$ can be determined with difficulty from analytical representations of $\epsilon''(\omega)$ and $\epsilon'(\omega)$ of the right form.

What is important is the significance of sets of relaxation times or continuous spectra of relaxation times. A discrete set can be regarded as a collection of times each of which represents a Debye-type equation and each of which contributes independently to the

polarisation. Some experimental systems have a reasonable molecular basis for representation by a set of discrete relaxation times e.g. figure 3(a) suggests the overlapping of three single relaxation processes.

The flat arc and skewed arc loci (figures 3(b) and 3(c)) correspond to broader dispersion regions and flatter absorption peaks than those for Debye-type relaxation. The circular arc locus is given empirically by

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_o - \epsilon_\infty}{1+(i\omega\tau)^{1-\alpha}} \quad \text{with } 1 > \alpha \geq 0$$

$\alpha = 0$ gives the Debye equation. The corresponding spectrum $F(\tau)$ is logarithmically symmetrical about $\tau = \tau_o$. For other systems which show broad absorption regions (figure 3(c)) there is more difficulty in finding molecular mechanisms which correctly predict spectra when a linear combination of simple differential equations is used. In these cases it appears that use of a linear combination of simple differential equations may not be justified and the resulting spectra of relaxation times are, therefore, of academic interest.

C.1.b.i: Relaxation in gases

In the case of gases at low pressures, theories assume that relaxation arises because the energy which the field imparts to the molecule is distributed to other degrees of freedom by collisions. As densities are increased this explanation becomes obscure since the molecules are almost continuously in a strong state of interaction. Models for dense gases consider the effect of the field on the probabilities of

transition between rotational states of the molecule, assuming that in the absence of the field all states are equally probable.

C.1.b.ii: Relaxation in liquids

Models for dense gases cannot describe liquids for two reasons. Firstly, it was pointed out earlier that consideration of single molecules in dense systems is not justifiable. Secondly, the assumption that all orientations are equally probable in the absence of a field neglects dipole interactions between molecules. Two problems arise when attempting to describe relaxation in polar liquids:

i) the satisfactory representation of an irreversible approach to equilibrium on a molecular level;
ii) the relation of the macroscopic external field to the local microscopic field when both are time dependent.

Debye's model: Debye assumed 'orientation diffusion' to occur in time dependent fields. Energy is dissipated in overcoming molecular 'friction'. A function f can be defined which gives the probability that a number dN of molecules are oriented in solid angle $d\varphi$ such that

$$dN = f\,d\varphi$$

The molecular friction is represented by a constant ξ such that

$h = \xi \frac{d\theta}{dt}$ where h is the torque and $\frac{d\theta}{dt}$ the angular velocity.

Continuity equations lead to the Schmolukowski equation

$$\xi \frac{\partial f}{\partial t} = \text{div}\,(kT\ \text{grad}\ f - Lf)$$

Debye used the Lorentz field as the local molecular field and put the torque L equal to

$L = -\mu E_L \sin(\theta)$ where (θ) is the angle between μ and E_L.

For a sinusoidal field f can be calculated to be

$$4\pi f = \frac{1+\mu E_L^{o}\cos(\theta)}{kT(1+i\omega\tau)}$$

and the molecular relaxation time is $\tau = \xi/2kT$. f can then be used to evaluate the mean moment and time dependent polarisation. The result is the Debye equation for the relaxation

$$\epsilon^* - \epsilon_\infty = \frac{(\epsilon o - \epsilon_\infty)}{1+i\omega\tau}$$ given above

Debye interpreted ξ by assuming that a dipole responds to a torque as a rigid sphere of radius a turning in a fluid of macroscopic viscosity η. Stokes' formula

$\xi = 8\pi\eta a^3$ then gives

$\tau = 4\pi\eta a^3/kT$.

Replacing ξ by η does, in fact, go no further in explaining the process but experimental results for η and τ can give reasonable results for a.

C.1.b.iii: Relaxation in solids

Debye's equation for the complex dielectric constant ϵ^* has been derived for solids as well as for liquids though using a different model. Broader relaxation regions involving a range of relaxation times may be described by Fuoss and Kirkwood's empirical relation.

$\varepsilon'' = \varepsilon''_{max}\ \mathrm{sech}(\alpha\ \mathrm{Ln}(\omega\tau))$ where f is frequency and α varies between 1 for a single relaxation time to 0 for an infinite range of relaxation times.

Diffusion models used to describe relaxation processes in liquids are not likely to be realistic models for relaxation in most types of solids. As mentioned earlier, models which are used for solids tend to consider a single dipole whose orientational movement is restricted by potential barriers. The dipoles normally have energies such that they may be considered to reside in potential troughs. Occasionally, due to thermal fluctuations, a dipole will possess enough energy to cross a potential barrier. In the absence of a field an equilibrium will exist such that over a large enough sample the distribution of dipoles in the available potential troughs is a constant. Application of a field will tend to change the distribution so that dipoles will tend to align themselves with the field.

Debye's Model: Debye assumed that each dipole possessed two positions of equilibrium equal in energy and separated by a potential barrier ΔE as in figure 4.

The dipoles oscillate about the equilibrium positions and occasionally acquire enough energy to cross the potential barrier to the other equilibrium position. With no field applied, the equilibrium positions are equally populated. When a field is applied some dipoles will rotate such that more dipoles occupy the position favoured by the direction of the field, thus polarising the sample.

The frequency of maximum absorption is given by

$$f_{max} = \frac{1}{2\pi\tau} = Ae^{-\frac{\Delta E}{RT}}$$

where A is a constant. In practice A varies and is sometimes written as an entropy term

$$f_{max} = \frac{fo}{\pi} e^{-\Delta S/R} e^{-\Delta E/RT}$$

where f_o is the frequency of oscillation of the dipole in the potential troughs (of the order of 10^{-12}/sec).

f_{max} can therefore be written as

$f_{max} = \frac{f_o}{\pi} e^{-\Delta F/RT}$ where ΔF is the free energy of activation.

Some authors apply absolute reaction rate theory which gives $\frac{kT}{h}$ instead of $\frac{f_o}{\pi}$. The values of ΔS and ΔF derived from this method agree, at room temperatures, with those from the above equation.

Debye's equation is not, in fact, restricted to a model with only two equilibrium positions of equal energy but applies to a model with any number of potential troughs of equal energy separated by potential barriers of equal energy. In such a system, the magnitude of the absorption increases with decreasing temperature.

In most solids the energies of the potential troughs are unequal as are the energies of potential barriers separating them. The linearity of a plot of Ln f_{max} versus $\frac{1}{T}$ gives an indication of how well Debye's model is approximated in the Temperature/Frequency range considered.

For a model in which there exists two troughs of unequal energy as in the diagram of figure 5, the molecular relaxation time is given approximately by the expression

$f_{max} = \frac{1}{2\pi\tau} = Ae^{-\frac{\Delta E_1}{RT}}$ where ΔE_1 is approximately the smaller energy barrier.

Clearly, this is a better approximation as $\Delta E_1 \longrightarrow \Delta E_2$ and Debye's model is more closely approximated.

The above two-site model gives one relaxation time. Two relaxation times are given by a slightly more complicated model. Extensions of the model to give three or more relaxation times have been made.

The magnitude of the absorption is not given by the expression relating f_{max} and T. Frohlich concluded that the two site model with equal energies can be described by an equation for the magnitude of the absorption in liquids. This type of equation is difficult to formulate but Onsager's formula for the dispersion

$$\epsilon'_o - \epsilon'_\infty = \frac{4\pi N_o \mu^2}{9kT} - \frac{\epsilon'_o(\epsilon_\infty + 2)^2}{2\epsilon' + \epsilon_\infty}$$

has been found to apply to a number of systems. For the two site model with troughs of unequal energies, the dispersion is given by

$$\epsilon'_o - \epsilon'_\infty = \frac{C}{T}\left(1 + \cosh\frac{\Delta E_o}{RT}\right)^{-1}$$

where C is a constant.

For $\Delta E_o >> RT$ this reduces to

$\epsilon'_o - \epsilon'_\infty = \frac{B}{T} e^{-\frac{\Delta E_o}{RT}}$ with B a constant.

Some polar solids e.g. long chain aliphatic ketones do not absorb at temperatures up to the melting point. This indicates that ΔE_o for the dipoles involved must be large.

Summary: The Dielectric Theory gives an adequate description of the equilibrium polarisation of gases at low pressures. For denser gases, liquids and solids, the problem involved in specifying properly the molecular processes responsible for equilibrium polarisation are such that models which may be of dubious validity have to be employed. In the case of dielectric relaxation which is essentially a non-equilibrium irreversible process, the difficulties of describing the responsible underlying molecular processes are even greater than in the equilibrium case. The result of this is that in the study of dielectric relaxation emphasis is shifted from attempts to apply detailed theoretical calculations to empiricism. Results may be compared with data obtained by other means and with data for the dielectric absorption of samples whose structure is known to be closely related to that of the sample under consideration. In this way a qualitative understanding of the process may emerge.

The position is closely paralleled by the state of knowledge of absorption in the infra-red. In this case detailed calculations can be successfully made for simple molecules. The infra-red spectra of complex molecules, however, are seldom subjected to any mathematical analysis which would be prohibitively complicated. The usefulness of the technique lies in the vast accumulation and correlation of qualitative results. In this respect studies of

dielectric relaxation suffer in that there does not exist the wide range of experience such as is available in the field of infra-red absorption.

C.2: Dielectric relaxation in polymers

The connection between the measured electrical properties and the molecular structure of a polymer cannot be simply expressed. The molecular structure is often not known exactly; small amounts of impurities may contribute to and even dominate the measurements; the sample may not be stable. Molecular mechanisms proposed to account for dielectric behaviour are the result of experience and a range of related data from studies using nuclear magnetic resonance, X-rays, optical properties, infra-red spectra, mechanical and thermal properties.

The detailed dielectric theory developed for simpler molecules generally breaks down when applied to polymers since the underlying assumptions are no longer valid. There are, however, semi-empirical relations which may be of use in analysing data. These include activation energy relations between the maximum frequency and temperatures, and relations which may estimate the spread of relaxation times characterising the process.

The dielectric properties of polymers depend on molecular relaxation processes which affect other properties, in particular mechanical properties. In general, polymers appear to be characterised by several distinguishable relaxation processes which can be attributed to the thermal motion of different molecular units. These may be side chains or pendant groups or portions of the main chain itself. When the movement of such a unit involves a change in

dipole moment, dielectric loss is exhibited. The movement of a unit may be characterised by a relaxation time or, if the movement is complicated, by a spectrum of relaxation times. Unfortunately, no complete theory exists which relates polymer structure to relaxation times and their temperature dependence. Hence the connection between dielectric properties and polymer structure tends to be made on the basis of experience and related experimental studies.

Experimental evidence indicates that, in general, linear polymers and lightly crosslinked polymers exhibit two types of dielectric relaxation. One involves movement of dipoles independently of the main chain and the other involves movement of a portion of the main chain with a dipole incorporated (i.e. the movement of dipolar segments of the main chain). In Mikhailov's[40] terminology, the former gives rise to 'dipole-radical' losses and the latter to 'dipole-elastic' losses. Dipole radical losses generally appear, in the frequency and temperature ranges normally studied, in the glassy state of the polymer, but this need not be the case. Mikhailov reports dipole-radical losses in polymethylmethacrylate at a frequency of 5 Mc/s at 190^{o}C, well above the glass-transition temperature at this frequency.

The characteristics of dipole-radical losses are closely connected with the immediate surroundings of the dipole and hence are independent of the movement of the main chain unless this specifically alters the surroundings of the dipole. This may occur in crystalline parts of the polymers where neighbouring chains are closely packed in a specific way or where there is interaction such as hydrogen-bonding between

different chains or portions of a chain.

Dipole-elastic losses are related to movements of the chain and are hence ultimately connected with the glass-transition temperature. It is clear, therefore, that the presence of plasticisers will substantially affect the characteristics of dipole-elastic losses while, in general, not affecting those of dipole-radical losses. Stretching likewise affects only dipole-elastic losses. Co-polymerisation may affect both types of loss.

Some evidence appears to indicate that the segments responsible for dipole-elastic losses cannot be very long and light crosslinking has no effect on dipole losses. Extensive crosslinking, however, limits the possibilities for segmental motion and hence profoundly affects dipole-elastic losses.

Roughly speaking, dipole-elastic losses and dipole-radical losses may be distinguished by plots of log f_{max} versus $\frac{1}{T}$ where f_{max} is the frequency of maximum absorption at temperature T. The former generally show apparent activation energies very much greater (40-120 k cals/mole) than the latter (5-30 k cals/mole). The mechanism providing for dipole-elastic losses is usually a complicated one and the apparent activation energy calculable, even if the log f_{max} versus $\frac{1}{T}$ plot is linear, is of dubious significance. These processes are usually characterised by a range of relaxation times.

Ferry's[24] method of reduced variables to determine the spectrum of relaxation times characterising a certain process involves the implicit assumption that the distribution function for relaxation times is independent of temperature, which in turn implies that all the elementary processes contributing to the

whole process have the same temperature dependence. This is not generally the case in practice and so the method is of limited applicability. A method of estimating the spread of relaxation times is from a Cole-Cole plot. If the locus of ε^* in the complex plane is a circular arc, α, the distribution parameter, in the expression

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_o - \varepsilon_\infty}{1+(i\omega\tau)^{1-\alpha}}$$

can be calculated.

Polymers may be divided into the two classes - linear/slightly crosslinked, and extensively crosslinked. There is little experimental data concerning the investigation of basic molecular structure in highly crosslinked systems. General theoretical discussions about the dielectric properties of such systems do not appear to exist. The first class may be divided into polar and non-polar polymers and these can be arbitrarily divided into crystalline and non-crystalline polymers. These types will be briefly described.

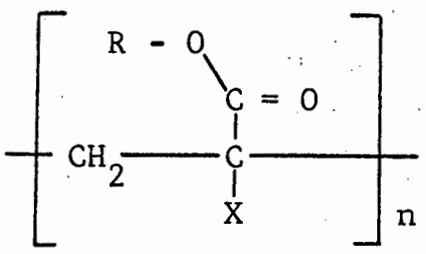
Non-polar polymers: As would be expected, non-polar polymers (e.g. polyethylene and polytetrafluoroethylene) are characterised by values for the dielectric constant which indicate that only electronic and atomic polarisations are effective, and by low values of tan δ. These are, however, not insignificant. For polyethylene, several well defined loss regions have been reported. Experimental studies (in particular infra-red investigations) have shown that the loss is due to extraneous carbonyl groups introduced during polymerisation or processing. Likewise in the case of

P.T.F.E., the very low dielectric losses are probably due to oxidation, impurities or end groups. Dispersion regions corresponding to phase transformations in P.T.F.E. have been reported.

Polar Polymers:

It is reasonable that the dielectric behaviour of crystalline regions in polymers would be different from that of amorphous regions in view of the different mechanisms which must be operative to provide for dielectric loss in each case. In particular, the glass transition is a characteristic of amorphous material while a well-defined melting point is characteristic of crystalline material, both transformations being accompanied by changes in dielectric properties. Dipole-radical losses may well be modified in crystalline material because of interaction between groups responsible for this type of loss.

Typical of amorphous polar polymers are the acrylics, which have been extensively studied. A general formula is



where both X and R may be varied. Polymethylmethacrylate has R = X = CH_3. It is clear that in changing R, the properties of the pendant group can be changed and by changing X, the properties of the polymer chain itself can be varied. Systematic studies have been made of polymers with differing X and R and some general characteristics have been brought to light. Generally,

the polymers exhibit two well defined loss regions termed α and β respectively. Perhaps the greatest benefit which has accrued from a systematic study has been a clear-cut distinction between the two processes. The α-peak has been characterised as due to dipole-elastic losses and the β-peak as due to dipole-radical losses. The dipole-elastic loss appears to be unambiguously related to the glass-transition temperature and the motion of segments of the main chain. The mechanism responsible for the β-peak is not so obvious, but the evidence indicates that it is due to motion of the ester side-group.

Dipolar motions which are possible in amorphous material may be inhibited or modified in crystalline material because of steric hinderance due to the close packing of polymer chains in the crystal or because of specific interactions between the dipoles which characterise the crystalline state. Dipolar movement may, however, be able to occur in the crystalline state of polymers just as it is possible in crystals of monomeric polar organic compounds.

D. Part I: Experimental

Part I describes the investigation of the dielectric properties of fully cured and increasingly degraded specimens of the adduct of the diglycidyl-ether of Bisphenol A and p,p'-diaminodiphenylmethane.

D.I.1: The starting materials

It was stated in the introduction that it was felt important to degrade a resin whose chemical structure was known as well as possible. For this reason a pure sample of the diglycidylether of Bisphenol A was cured with pure p,p'-diaminodiphenyl-methane.

The diglycidylether (dge-BPA) was recrystallised from a commercial sample of the crystalline material (Ciba EP274) according to a method recommended by the manufacturers.* The recrystallisation was from an ethanolic solution of the commercial material and, after filtering, the recrystallised product was dried under vacuum for several days.

Relatively large crystals (approximately 1 m.m. long) could be grown from a melt of the dge-BPA. The crystals melted over the range 39-42°C, complete melting occurring only at 42°C.

Elemental analyses of the dge-BPA gave the following results:

Experimental:

%C	%H	%O	%N	%Cl
73.76	7.22	18.41, 18.56	0	.61, .46
73.92	7.00	18.78, 18.70	0	.30, .38

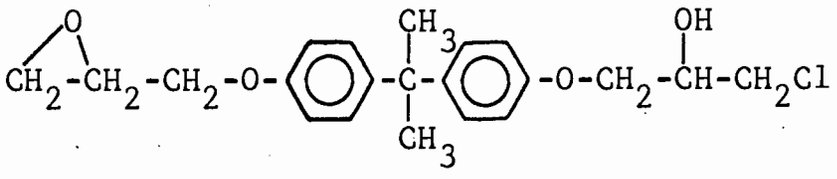
Theoretical:

74.08	7.105	18.8	0	0

*Private communcation.

In the preparation of discs, the solid dge-BPA was always melted and evacuated before being weighed finally. A typical weight loss due to evacuation for 20 minutes was 0.1%.

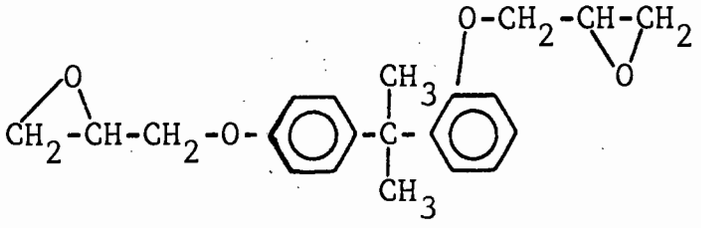
The most likely reason for the chlorine content is the presence of molecules with the structure



I

in which ring closure to form one of the terminal epoxide groups during the synthesis of the dge-BPA from epichlorhydrin and Bisphenol A has not been successful. Calculations based on the figure of 0.4% chlorine showed that, if all the chlorine present were due to this substance then for every 1,000 molecules of the dge-BPA there were present in the resin some five molecules with the above formula.

The manufacturers stated* that molecules of the form



are present in the original material in 1-2% quantities. Recrystallisation may have reduced this quantity.

In summary, the resin used in the preparation of discs was a fairly pure sample of the diglycidylether of Bisphenol A. Chlorinated molecules (I) are present in some ½% mole ratio, and isomeric molecules (2-4'-

*Private communication

disubstituted instead of 4-4'-disubstituted) in some 1% mole ratio.

The hardener, p,p'-diaminodiphenylmethane (DDM), was recrystallised from a solution in hot water of a commercial product. Elemental analyses of the recrystallised product gave

Experimental:

%C	%H	%N	%O (by difference)	%Cl
78.13	7.15	14.16	.27	.29, .29
78.50	7.00	14.52	0	

Theoretical:

78.70	7.11	14.13	0	0

D.I.2: Preparation of discs

The preparation of the discs used in the dielectric studies was as follows:

A sample of the recrystallised dge-BPA was weighed out. It was melted and evacuated for 20 minutes. The weight was taken again and the weight loss due to evacuation calculated. This was never greater than 0.1%. A weight of DDM calculated as 28.8% of the final weight of the dge-BPA was added. The mixture was heated until a mobile, homogeneous liquid resulted. This was then evacuated for 20 minutes to rid the mixture of air bubbles. After evacuation, the mixture was again weighed - a typical weight loss figure was 0.1%. Elemental analyses showed that evacuation of the mixtures had no significant effect on the C:H:O:N ratios i.e. neither component was significantly more volatile than the other. The mixture was then heated till mobile and cast in polythene moulds which were air tight. The resin was cured for approximately 20 hours at a temperature of 95^{o}C. The resulting discs were honey-coloured, circular, of diameter approximately 5½ cms., and approximately 0.13 cms. thick. After filing off extraneous matter, the discs were weighed before cure/degradation under low pressure.

D.I.3: Post-cure and degradation

Post-cure and degradation were performed at low pressure (of the order of 0.7 mm. of mercury) to prevent oxidation. In fact, post-cure and degradation were not distinguished for reasons explained fully in section F. The discs of resin which had been cured at 95°C were weighed and then clipped with 'Bulldog' clips onto a flat clean aluminium plate to avoid distortion during heating, care being taken that the clips did not come into contact with any portion of the disc which would be subsequently situated between the electrodes of the cell used for dielectric measurements. This assembly was placed in the degradation vessel shown in figure 6.

The vessel was sealed by bolting the cap on. The copper gasket was compressed by a lip on the reaction vessel into a groove in the cap thus providing a seal. The reaction vessel was connected by rubber pressure tubing to the glass-apparatus shown in figure 7.

The first trap was for condensible products produced during degradation. The second trap served to prevent back diffusion of oil vapours from the pump into the first trap.

The procedure for the post-cure/degradation of a sample was as follows:

(1) The discs of resin were weighed, clipped to the aluminium plate and introduced into the reaction vessel which was then closed and connected via the traps to the pump.

(2) The whole apparatus was pumped down with taps T1, T2, and T3 open. Meanwhile the traps were immersed in liquid air. The pressure was read periodically and, when a minium (usually after a few minutes pumping), it was noted and tap T2 shut.

(3) The reaction vessel was introduced into an oven at the desired temperature and the time noted. The temperature of the reaction vessel was continuously monitored by a chromel-alumel thermocouple connected to a recording potentiometer with the cold junction at $0^{o}C$. The thermocouple gave the temperature of the outside of the reaction vessel.

(4) Pumping was continued and the temperature monitored for the duration of the post-cure/ degradation.

(5) At the desired time, the reaction vessel was removed from the oven and taps T1 and T3 shut.

(6) The discs were removed from the cooled reaction vessel and were both weighed to determine weight loss and physically examined.

D.I.4: Dielectric Measurements

The dielectric properties of the resin discs were measured at nine fixed frequencies in the frequency range 210 c/s to 90 kc/s and in the temperature range of approximately -180°C to 240°C. The discs formed the dielectric of a parallel plate capacitor, or cell, whose capacitance and loss were measured on a dielectric bridge.

The construction of the cell is given in figure 8.

The resin disc was placed between two electrodes of aluminium with flat machined faces. One electrode was circular, of diameter some 5.5 cms.; the other electrode was circular with diameter accurately 3.1 cms., surrounded by an anular guard ring approximately 1 cm. wide. The electrodes were cemented to bakelite plates which were backed with steel plates so that the whole assembly could be bolted together without distortion of the electrodes. The steel backing plates and bolts were all earthed. Terminals from the electrodes and guard ring were connected to the bridge by means of leads insulated with PTFE and each sheathed in a copper spiral to elininate mutual capacitance effects. After measurements at high temperatures the bakelite plates showed evidence of degradation. Tests proved, however, that their insulation was in no way impaired.

The dielectric bridge used in the measurements was designed and built by Baker (AEI.Ltd.). The circuit diagram is shown in figure 9.

X was the lossy capacitance to be measured. S was a standardised variable capacitor. R is a variable resistance and C a variable capacitance

and a voltmeter with a range 1 mV to 10V was necessary for the detector.

At balance X = S and the loss tangent

$\tan \delta = \omega rk = \omega RC = 2\pi fRC$ where f is frequency in c/s.

S was standardised by comparing it with known capacitances. In this way a proportionality factor between readings on S and capacitance was found. The absolute capacitance of S, including the self and mutual capacitance of the leads to the cell was measured by substituting various standard non-lossy capacitances (accurate to 1%) for the cell and balancing the bridge. In this way the capacitance of the cell was related to readings on S. The standardisation was important as the self-capacitance of the leads was of the order of the capacitance of the cell (several pF).

The dielectric constant of the resin disc was calculated using the standard equation for the capacitance of a parallel-plate condenser

$$C = \frac{\epsilon \epsilon_o A}{d}$$

C = capacitance in farads
A = area of electrode in m^3
d = width of dielectric in m.
ϵ_o = absolute permittivity
ϵ = dielectric constant

This was considered to give accurate enough values of ϵ since a guard-ring was used and very accurate values of ϵ were not required. Values of the loss tangent were given directly from readings of R and C on the bridge.

For readings in the temperature range - 185°C to room temperature the cell was wrapped in two separate layers of polythene sheeting which prevented

condensation of water from the atmosphere onto or into the cell. The wrapped cell was placed in a massive iron cylinder of very high heat capacity which was cooled to liquid air temperatures and placed in a thermos flask. Readings at temperatures between liquid air temperatures and room temperatures were taken while the cell and cylinder heated up slowly to room temperature. The maximum rate of temperature rise was less than $1^{o}C$/minute which enabled the bridge to be balanced easily. Values of ϵ calculated from these readings were not strictly isothermal but the rate of temperature change was such that the difference between the experimental values and isothermal values of ϵ was negligle. For readings at temperatures greater than room temperature the cell was placed in an oven which maintained the temperature between $\pm$ $1^{o}C$ of the desired value. Helium was circulated around the cell for readings at temperatures greater than $140^{o}C$ to prevent any oxidation of the resin discs. Examination of the discs after dielectric measurements had been taken showed that some slight superficial darkening had occurred. The extent of this was such that it did not affect the results.

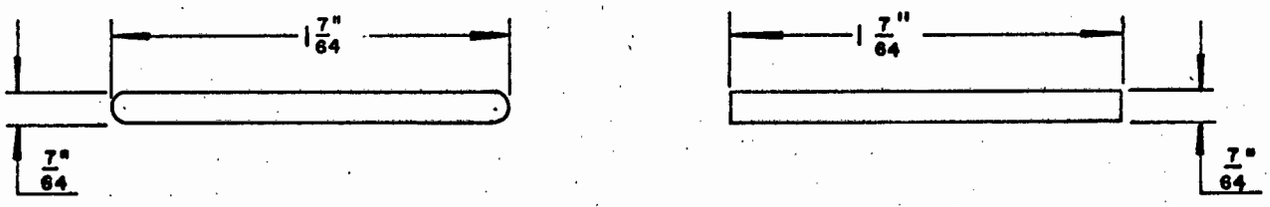
The temperature of the cell was measured by measuring the E.M.F. of a chromel-alumel thermocouple with one junction sunk into one of the bakelite plates of the cell and the other maintained at $0^{o}C$. Temperature variations across the sample were likely to be minimal as the electrodes and steel backing plates would serve to even out any temperature variations. Heating of the dielectric due to the measurement was negligible.

D. Part II: Experimental

Part II describes the investigation of the reaction products resulting from the degradation of the adduct of the diglycidylether of Bisphenol A and p,p'-diaminodiphenylmethane.

D.II.1: The starting materials

The diglycidylether of Bisphenol A and the p,p'-diaminodiphenylmethane used in experiments on the degradation products were from the same samples as those used in the dielectric studies (section D.I.1).



Plan

Side

FIGURE 10. Resin Bars

D.II.2: Cure

Approximately 40 g. of the dge-BPA were weighed out and melted in a glass beaker. The melt was evacuated for 20 minutes. The percentage weight loss following evacuation was 0.037%. A quantity of DDM calculated as 0.2912 of the weight of the dge-BPA after evacuation was added. The mixture was heated and stirred to obtain a homogeneous solution. No weight loss followed the heating and mixing. The liquid was again evacuated to remove air entrapped during stirring. The percentage weight loss following evacuation was again 0.037%.

The resin was cured in the form of small bars. The shape and dimensions of the bars are shown in figure 10. The mould consisted of a 12" square sheet of ¼" thick polythene out of which had been machined slots corresponding with the shape of the bars. The melt was poured into the mould and cured for 210 minutes at 94°C. Since a feature of the degradation apparatus used in Part II was that the final temperature of degradation was reached far more rapidly than was the case in experiments described in Part I, the bars were removed from the mould and given a post-cure of 30 minutes at 165°C. The temperature of the initial cure was chosen as 94°C since this was the highest temperature practicable without causing distortion or melting of the polythene mould. Post-cure was performed at 165°C because at any higher temperature oxidation of the resin becomes appreciable.

Polythene is an ideal mould material for epoxy resins because no release agent, which in the present case may have caused contamination of the resin, is necessary. In addition the polythene contained no

plasticisers which might also have caused contamination of the resin.

Figure 11. Degradation Apparatus

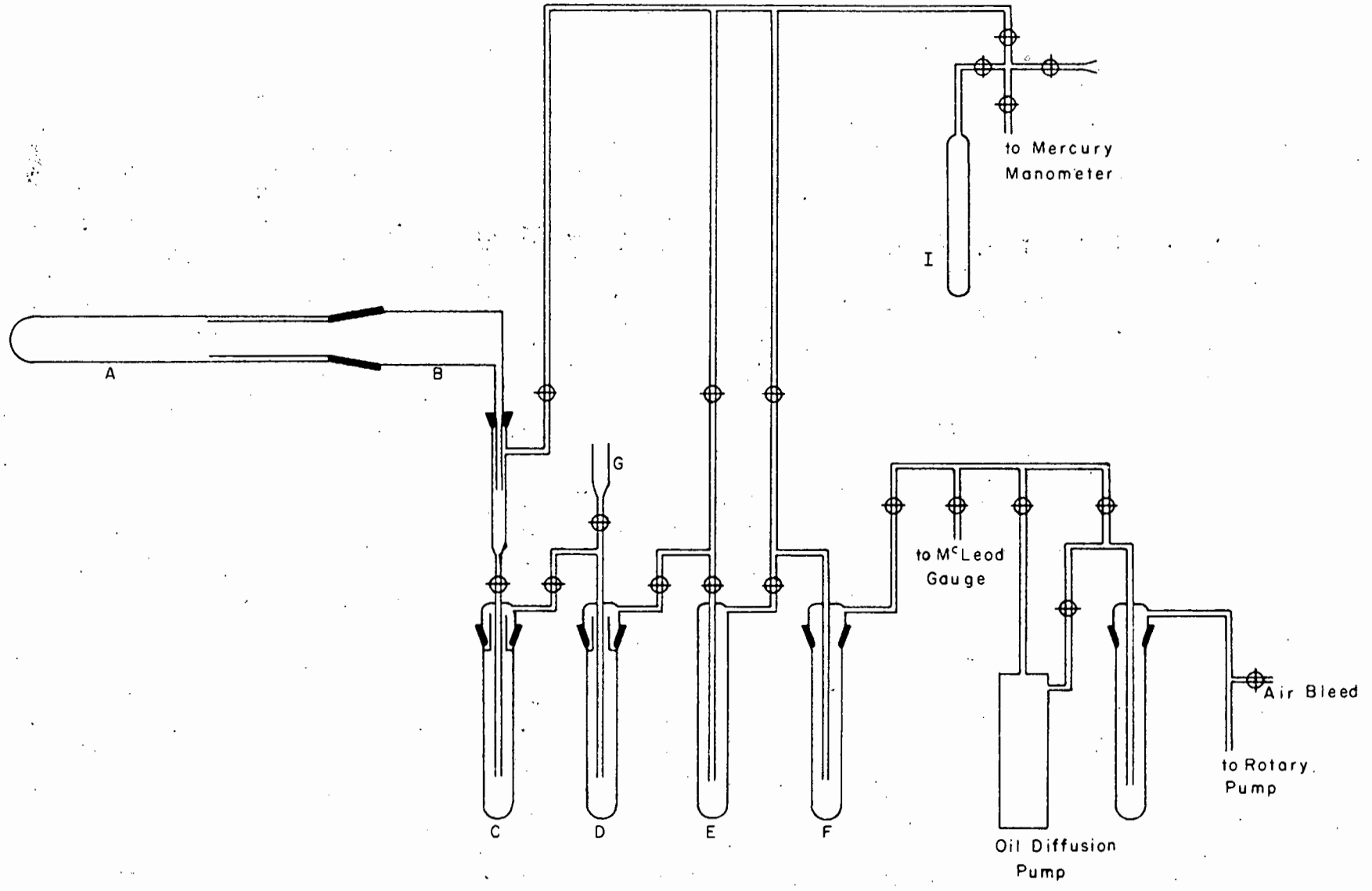


FIGURE 12. Degradation Apparatus

D.II.3: Degradation apparatus

A photograph of the degradation apparatus is shown in figure 11.

D.II.3.a: Vacuum line

The apparatus used for the degradation of the discs used in the dielectric studies suffered the weakness that only moderate vacuum could be achieved. The low pressures achieved during degradation of the discs were such that their oxidation was precluded but, despite this, during degradation quantities of air were pumped through the system. For the work on the degradation products it was necessary to use an all glass high vacuum apparatus to exclude air.

A schematic diagram of the apparatus is shown in figure 12.

The reaction vessel A was a pyrex glass tube 11" long and 1½" in diameter and was sealed at one end. This was connected by means of a B40 ground glass joint to the fore-tube B. The fore-tube extended 4½" into the reaction vessel. The length of the reaction vessel was such that with the heater tube in position surrounding it, the ground glass joint was sufficiently far from the heater to prevent melting of the silicone grease on the joint. The purpose of extending the fore-tube into the reaction vessel was to prevent low volatility reaction products from condensing onto or near the ground glass joint.

The fore-tube led to a series of traps. Traps C and D were detachable and were designed so that when reaction products were dissolved out, the resulting solution was not contaminated with grease from the

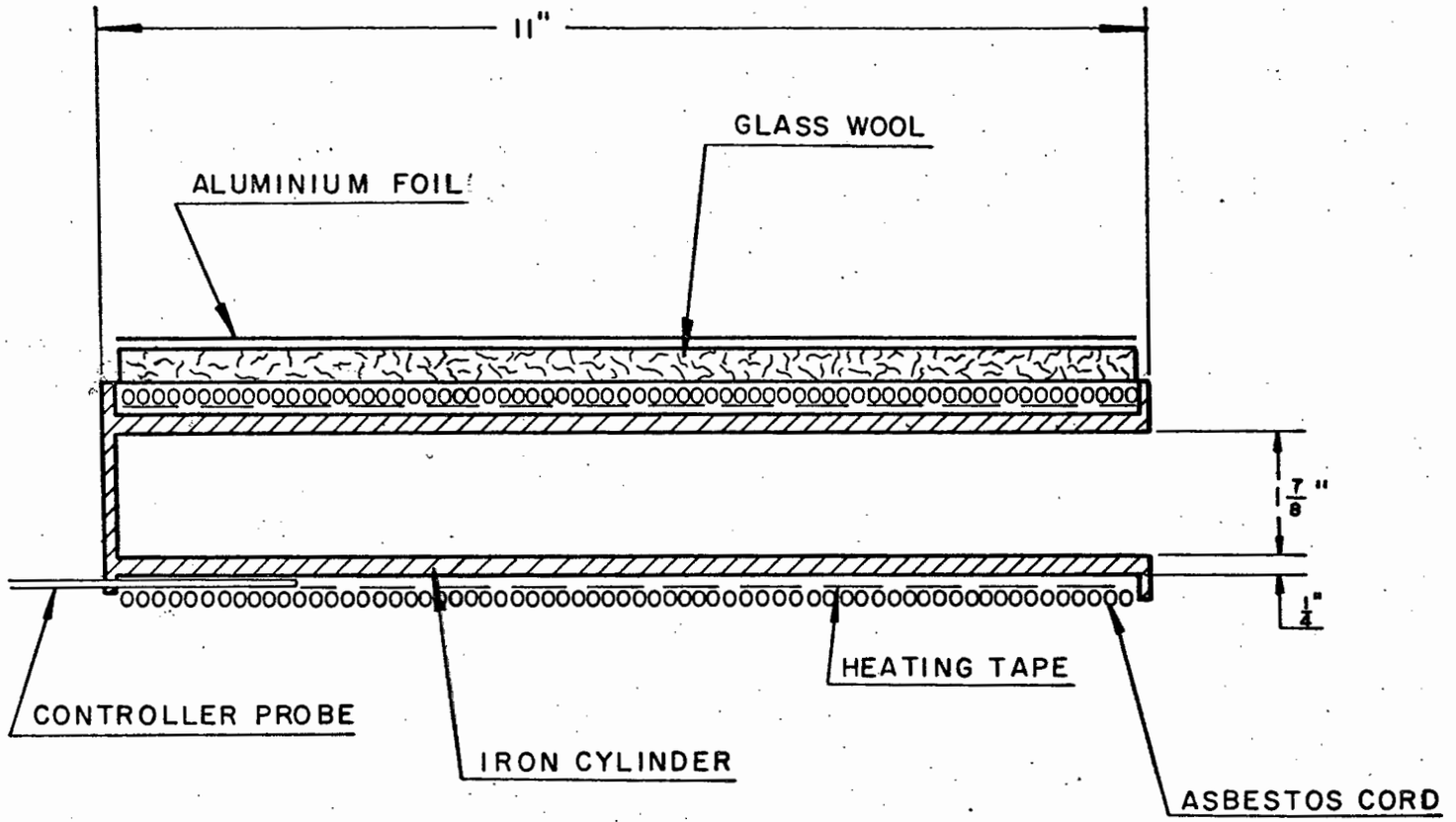


FIGURE 13: Heater Tube Construction

ground glass joints. G was a small reservoir such that solvent could be let into trap D directly. It was possible that after degradation this trap might have contained appreciably volatile products. The purpose of the reservoir G was to allow solvent to be admitted to the trap while it was still cooled and under vacuum so that solution of the products collected in the trap after degradation could occur before their evaporation. In fact, analysis of the solution showed that no very volatile products were present so that this facility was not strictly necessary.

Trap E was not detachable and was used to collect gaseous degradation products. Traps F and H were used to prevent back diffusion into the apparatus of oil vapours from the oil diffusion pump and rotary pump respectively. Traps C, D and E were connected to a reservoir I. This reservoir was used to store the gaseous degradation products from Trap E. Samples of gas from the reservoir at pressures measured on the mercury manometer could be removed for analysis.

Low pressures were measured by means of the McLeod gauge. A reservoir (not shown) was provided so that the McLeod gauge could be evacuated without using the rotary pump directly. Another reservoir (not shown) was provided on the backing side of the oil diffusion pump so that evacuation by this pump could continue while the rotary pump was used for other purposes.

D.II.3.b: Heater

The heater was effectively a tube furnace which could be moved onto and off the reaction vessel. Its construction is shown schematically in figure 13.

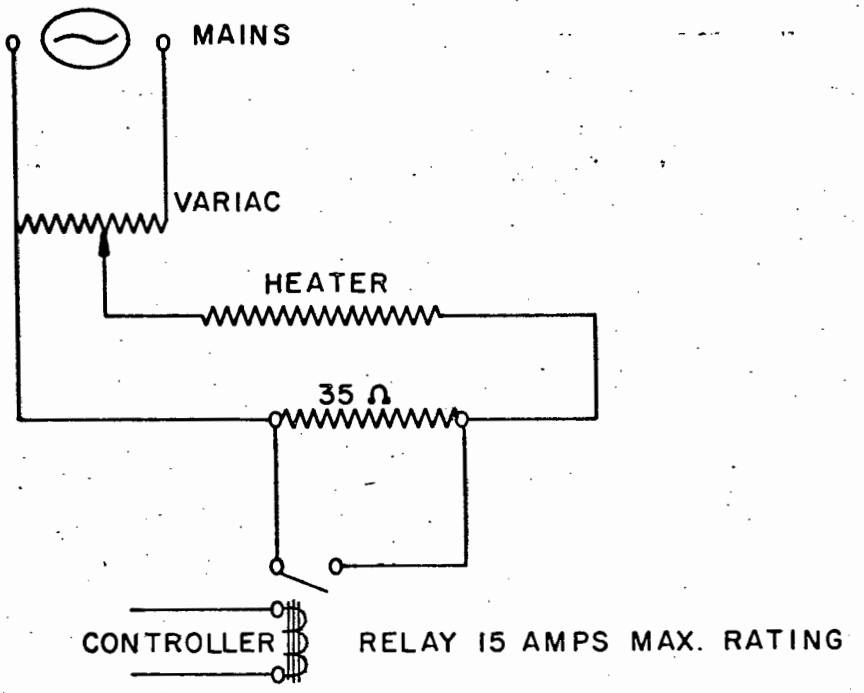


FIGURE 14: Heater / Controller Circuit.

A massive iron cylinder 11" long, of internal diameter $1\frac{7}{8}$", with a wall thickness of $\frac{1}{4}$" and sealed at one end was wrapped circumferentially with a heating element. This consisted of a tape element insulated with glass cloth, 6 feet long and rated at 1300 watts. Between the cylinder and the heating tape was placed the probe of the temperature controller. To keep the tape in position the assembly was wrapped with asbestos cord. Around this assembly was wrapped alternate layers of glass wool and aluminium foil. The final assembly was placed symmetrically in a metal box measuring 15" x 6" x 6". Any remaining crevices were filled with glass wool. The insulation was such that with the inside of the heater tube at a temperature of some 300°C the exterior of the heater could be handled with ease.

An asbestos plug sealed the open end of the heater tube during its warming up to the required temperature. The temperature controller* was a simple cross-coil instrument fed by a platinum resistance thermometer temperature probe of resistance 10 ohms. Its action was simply to activate a relay when the measured temperature exceeded a pre-set value and to deactivate the relay when the measured temperature dropped below the pre-set value. The range of the controller was 200°C to 300°C. The sensitivity and accuracy were quoted by the manufacturers to be 0.25% of full scale range viz. 0.25°C.

A schematic diagram of the heater/controller circuit is shown in figure 14. The heating element was fed by a Variac variable voltage transformer. In series with the heating element was a 35 ohms

*Ferris 891626P

resistance rated at 10 amps. When the relay was activated by the controller, the short-circuit of the resistor was broken and consequently the current flowing through the heating element was reduced. Deactivation of the relay short-circuited the resistance and the current flowing through the heating element increased.

Basically the circuit provided for a constant current to be fed to the heating element. This was controlled by the Variac to be just not sufficient to maintain the required temperature. An additional current could be switched in or out by the controller by means of removing or introducing an additional resistance into the heater circuit. In this way a fairly fine control was achieved.

During the warming-up period of the heater full mains voltage was applied to the windings to reduce the time required. The voltage was switched to a predetermined value just before the controlling temperature was reached.

Since the temperature probe was placed between the heating element and the cylinder, the controlling temperature was not the same as the temperature inside the heater tube. The value of the arrangement was that the large heat capacity of the cylinder served to dampen temperature fluctuations on its outside surface so that the temperature inside the cylinder remained practically constant.

The heater tube was switched on 5½ hours before its use. Experiments showed that it stabilised at the required temperature 2 hours after switching on. Experiments were performed to determine the constancy of the temperature inside the heater tube after its

stabilisation at the required temperature. In these experiments the reaction vessel was inserted into the heater tube and the temperature inside the reaction vessel was measured by means of a Copper/Constantan thermocouple probe. The cold junction of the thermocouple was maintained at a temperature of $0^{o}C$ by its immersion in melting ice. The E.M.F. of the thermocouple was measured on a digital voltmeter with a sensitivity of 0.01 mV and an accuracy of 0.01 mV which corresponded with a temperature variation of $0.1725^{o}C$. The digital voltmeter sampled the temperature at 5 seconds intervals. The results showed that the temperature inside the reaction vessel varied by amounts within the sensivity of the voltmeter i.e. within $\pm$ $0.1725^{o}C$. The long term stability (over 10 hours) of the temperature was also within these limits.

Experiments were carried out to determine the longitudinal and lateral temperature profiles of the heater tube. The experiments showed that lateral displacement of the reaction vessel in the heater tube produced no detectable change in the temperature inside the reaction vessel. The temperature variations along the heater tube were appreciable. An optimum position was found such that with the reaction vessel inserted 9½" inside the heater tube there existed a region of the reaction vessel extending 1½" from its end over which the temperature varied by less than $2^{o}C$. This region was used to contain the resin bars during their degradation.

Further experiments were carried out to determine the rate at which the reaction vessel heated up when it was inserted at room temperature

into the previously stabilised heater tube. The results of a typical experiment are summarised in table 1.

Table 1: Rate of heating of reaction vessel

Time (Minutes)	Temperature ^{o}C
0	25.5
5	261.6
10	286.5
20	293.5
30	298.1
40	302.6
50	303.9
60	304.2
90	304.1
120	304.2

It is clear that the degradations were by no means isothermal because of the appreciable heat capacity of the reaction vessel.

Finally, the rate of heat up of the resin bars was investigated. An idealised one-dimensional system was studied. An infinitely long cylinder of resin of finite radius s at constant temperature t_i was assumed to be placed instantaneously in contact with an infinite heat source at a constant temperature t_s. The temperature difference θ at a distance r from the centre of the cylinder at time τ is given by (Jakob[31])

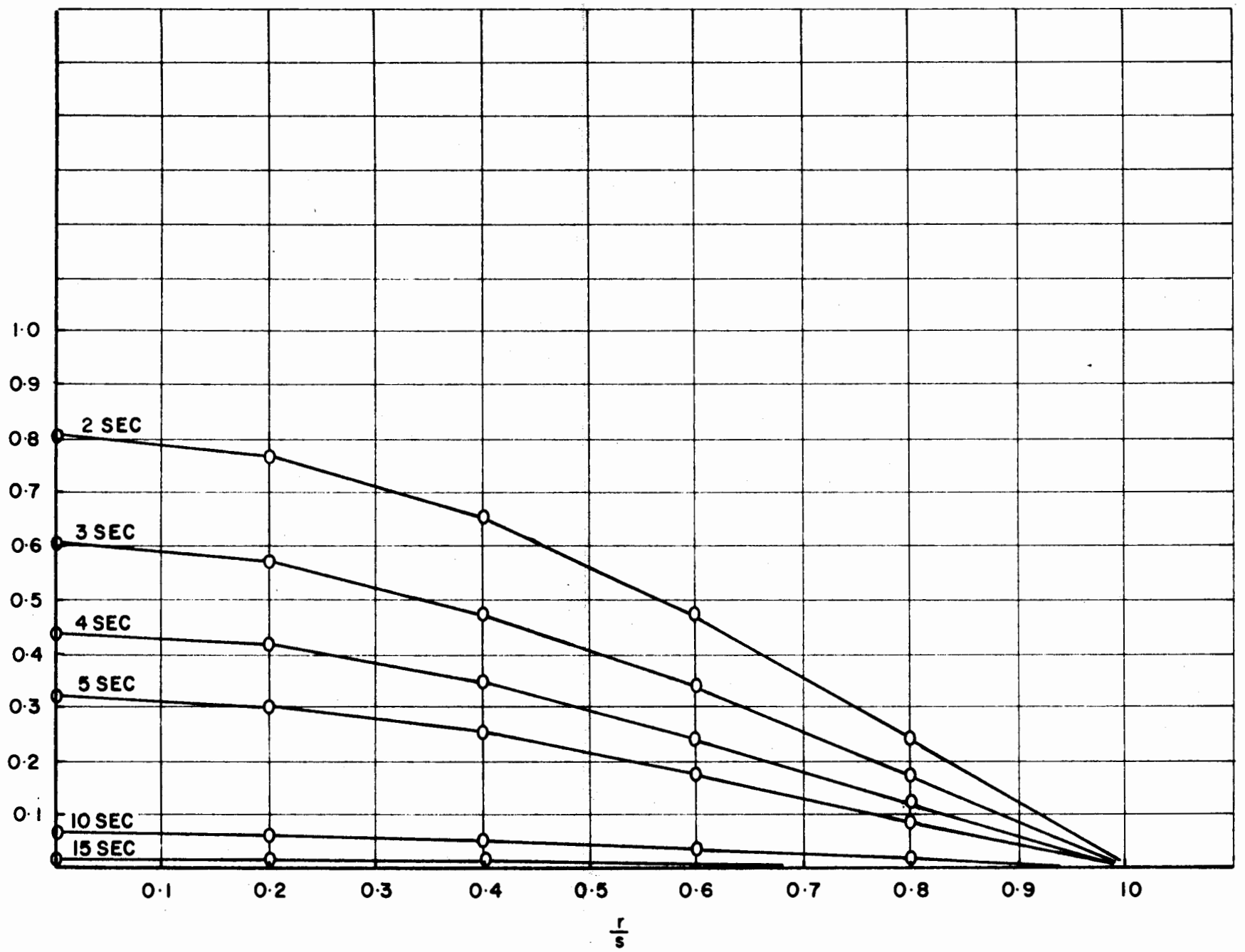


FIGURE 15 : Plot of $\frac{\theta}{\theta i}$ against $\frac{r}{s}$

$$\theta = \theta i \sum_{\psi=1}^{\psi=\infty} \frac{2}{\beta_\psi \, J_1(\beta_\psi)} e^{-(\beta_\psi^2 \alpha \tau / s^2)} \times Jo(\beta_o \frac{r}{s})$$

where Jo = Bessel function of the 1st kind and zero order

J_1 = Bessel function of the 1st kind and 1st order

β_ψ = the ψth zero place of Jo

θ = $t - t_s$
where t is temperature at any time τ and t_s is temperature of surface

θi = $t_i - t_s$
where t_i is initial temperature

α = the thermal diffusivity

τ = time

and r = distance from centre of cylinder.

The equation was solved numerically using a value for the thermal diffusivity of 0.0002 in ^{2}/sec. This value is an approximate value for epoxy resins at room temperature. Data at high temperatures for the resin/hardener system studied were not available. The calculation, however, afforded a qualitative guide to the rate of heat up of the resin bars. The results of the computation are shown in figure 15 which plots $\theta/\theta i$ against r/s at various times. It is at once clear that the time taken to heat the resin bars up to temperature is negligible compared with the time lag of the reaction vessel so that the temperature of the resin bars can be said to follow the temperature of the reaction vessel closely.

D.II.4: Degradation procedure

A quantity of the resin bars was weighed out accurately into the reaction vessel. The reaction vessel was connected to the degradation apparatus which was pumped with the diffusion pump for 5½ hours to remove air, particularly that adsorbed onto the resin. When a sufficiently high vacuum had been obtained, the degradation line (reaction vessel, fore-tube, relevant traps and diffusion pump) was isolated from the rest of the apparatus. A freezing mixture (22.1% ethyl alcohol in water) was used to maintain trap C at a temperature of -12.2°C during degradation. A dry-ice/acetone freezing mixture maintained trap D at a temperature of -77°C and liquid nitrogen was used to maintain trap E at a temperature of -196°C. The heater tube was placed in position and the time noted. Heating was continued for the required time. At the end of this period the heater tube was removed from the reaction vessel. Pumping was continued until the reaction vessel was cool. Traps C,D and E were each isolated.

The gaseous degradation products were distilled into the reservoir I by maintaining the latter at liquid nitrogen temperature while warming the trap E to room temperature. The reservoir I was isolated and maintained at a temperature of -196°C. Samples of the gaseous degradation products were removed for analysis (infra-red spectrum, mass spectrum and 2,4-dinitrophenylhydrazone formation) by warming the reservoir to room temperature and bleeding off the required pressure. The attainment of room temperature before sampling was necessary to avoid sampling only the more volatile species.

Solvent was admitted to trap D while it was still under vacuum and at a low temperature. The trap was warmed up to room temperature and detached. The solution in the trap was reserved for analysis. Air was admitted to the reaction vessel, fore-tube and trap C from the back line. The degradation products which had collected in the fore-tube and the trap C were dissolved and their solutions removed for analysis. Small quantities of degradation products which had collected in the reaction vessel were dissolved out, the degraded resin bars being washed with solvent simultaneously. The solution was added to the fore-tube solution. The degraded resin was dried under vacuum and reweighed.

D.II.5: Analytical methods

D.II.5.a: Gas chromatography

Gas chromatography was used extensively both as a separative technique and also, by means of comparisons of retention times of unknowns with those of standard chemicals, to provide confirmation of the identification of unknown products. A Pye* series 105 model 15 automatic preparative gas chromatograph was used in all the work. This instrument has facilities for temperature programmed operation and for the collection of materials from the column. By means of a splitter situated at the outlet end of the column, 1% of the carrier gas stream is led to the flame ionisation detector while the remaining 99% is led to the collection device.

Three columns were used. The first was a 15 feet long by ⅜" diameter glass preparative column packed with 25% polyethyleneglycol PEG 20M* on 60-72 mesh silanised Celite*. This column was particularly useful for the separation of fairly volatile products e.g. phenol, N-methylaniline, N,N-dimethylaniline and benzofuran. The polar nature of the column provided an easy separation of such compounds. The other columns used were 7 feet long by ⅜" diameter glass preparative columns packed with 15% and 25% respectively E30* methyl silicone gum on 60-72 mesh silanised Celite*. These columns were useful for the separation of fairly high molecular weight components of the degradation products. Whereas the PEG column was limited to a maximum operating temperature of 175°C the E30 columns were useful at temperatures up to 280°C. Data on retention volumes are collected in table 2.

*Trade name

Corrected retention volumes are quoted. The corrected retention volume is related to the measured retention time by

$V_c = f\ (t - t_s)$ where

V_c = corrected retention volume

f = flow rate of carrier gas

t = measured retention time

t_s = retention time of solvent.

Normally, retention times are measured from an air peak. Since the flame ionisation detector does not respond to air, the solvent peak (diethylether peak) was chosen as the datum. The retention of the column of the diethylether at the temperature involved is, in practice, negligible so that the relation is justified.

Table 2: Corrected retention volumes

Column: 15' x ⅜" diameter glass packed with 25% PEG 20M on 60-72 mesh Celite*	
Operating Temperature: 176°C	
Carrier Gas Flow Rate: 162 mls./min.	
Retention Time of Solvent (diethylether): 2 min. 37 sec.	
Compound	Corrected Retention Volume (mls.)
benzofuran	2.18×10^3
N,N-dimethylaniline	2.55×10^3
N,N-dimethyl-p-toluidine	3.16×10^3
N-methylaniline	4.53×10^3
N-methyl-p-toluidine	5.26×10^3
phenol	11.11×10^3

*Trade name

D.II.5.b: Infra-red spectra

Infra-red spectra were used both to characterise products whose spectra were readily identifiable and also as a diagnostic aid in the elucidation of chemical structure.

The instrument used was a Perkin-Elmer* model 457 grating spectrophotometer scanning from 4000 $cm.^{-1}$ to 250 $cm.^{-1}$ The maximum resolution of the spectrometer is quoted as 2 $cm.^{-1}$ at 3000 $cm.^{-1}$ and 1 $cm.^{-1}$ at 1000 $cm.^{-1}$

Infra-red spectra of gaseous compounds were measured by means of a 10 cm. path length gas cell with sodium chloride windows. Spectra of liquid compounds were measured on smears of the compound between sodium chloride plates. Spectra of solids were measured by the potassium bromide disc method. In this method a small quantity of the compound (of the order of 2 mg.) was ground with approximately 120 mg. of potassium bromide in an agate mortar. The well dispersed mixture was compressed in a die to a pressure of 8 $tons/in.^2$ to produce a disc. This method obviates the disadvantage of dissolving solid substances to determine the infra-red spectrum of their solutions (namely the absorbance of the solvent) since the potassium bromide matrix is transparent in the infra-red to 260 $cm.^{-1}$ In addition, spectra of crystalline substances often showed better resolved peaks. The infra-red spectra of the resin before and after degradation were determined by incorporating fine filings of the resin in a potassium bromide disc.

*Trade name

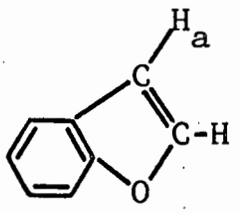
The infra-red spectra of the more common compounds, namely methane, ethane, ethene, chloromethane, carbon dioxide, carbon monoxide, acetaldehyde, acetaldehyde 2,4-dinitrophenylhydrazone, phenol, N-methylaniline, N,N-dimethylaniline, N-methyl-p-toluidine and N,N-dimethyl-p-toluidine are not quoted. The spectra of other degradation products, of the diglycidylether of Bisphenol A and p,p'-diaminodiphenylmethane, of the resin before and after degradation, and of the gaseous degradation products are collected in Appendix B.

D.II.5.c: Nuclear magnetic resonance spectra

Nuclear magnetic resonance spectra were used largely for the elucidation of chemical structure and to provide confirmation of a suspected structure. The determinations were made on a Varian A60 Analytical NMR spectrometer. The solvent used in all cases was deuterated chloroform. NMR spectra are collected in Appendix C.

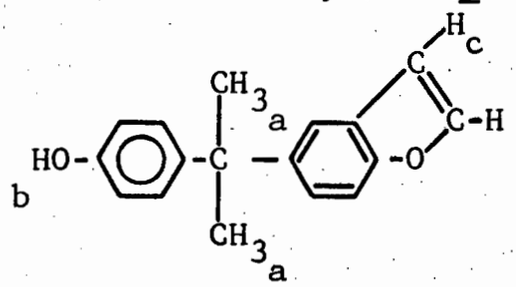
Assignments of the resonance peaks are as follows:

(i) Benzofuran:



a : τ = 3.42

(ii) 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane:

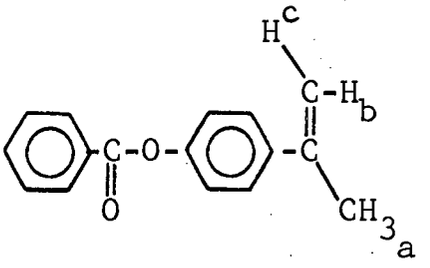


a : τ = 8.31

b : τ = 4.75 (peak disappears with D_2O exchange)

c : τ = 3.33

(iii) p-isopropenylphenyl benzoate:

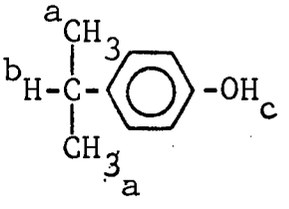


a : τ = 7.85

b : τ = 4.95

c : τ = 4.69

(iv) p-isopropylphenol:

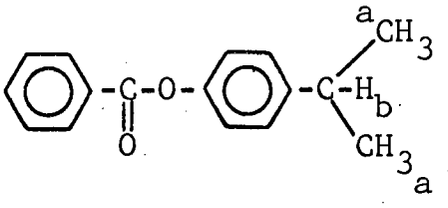


a : τ = 8.87, 8.77

b : τ = 7.41, 7.3, 7.19, 7.08

c : τ = 3.88 (peak disappears with D_2O exchange)

(v) p-isopropylphenyl benzoate:



a : τ = 8.81, 8.69

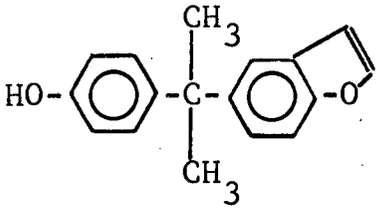
b : τ = 7.2, 7.19, 7.09, 6.96

D.II.5.d: Mass spectra

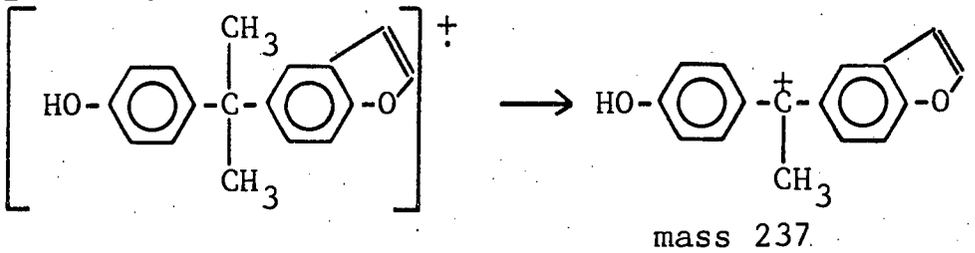
Mass spectra were used for the elucidation of chemical structure and also provided the primary analysis of the gaseous degradation products. An accurate mass determination of the molecular ion of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane provided a confirmation of its chemical formula.

A discussion of individual spectra follows. A discussion of the mass spectrum of the gaseous degradation products is reserved for section E.II.3.a.i.. Mass spectra are collected in Appendix D.

(i) 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane:

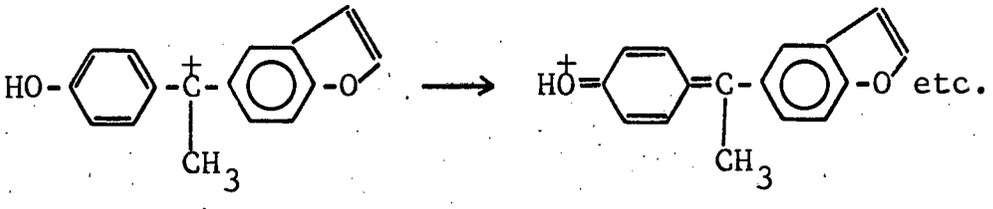


The mass spectrum shows three major peaks - the base peak of mass 237, the molecular ion peak of mass 252 and a small peak of mass 119. The primary process is loss of a methyl radical from the isopropyl group to form a stable ion:

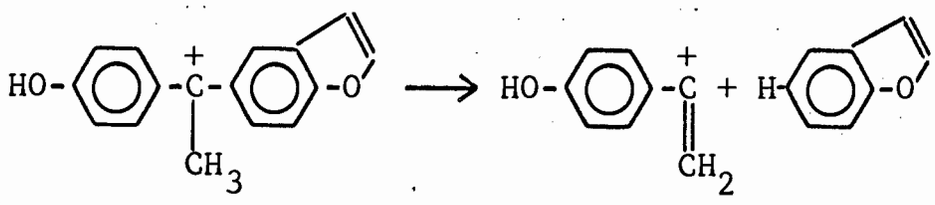


mass 237

This ion is stabilised by resonance:

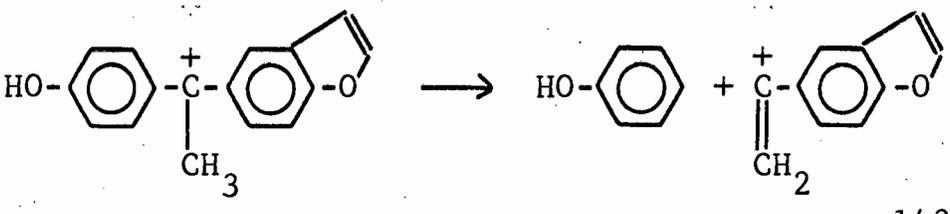


A secondary process appears to involve the loss of benzofuran:



mass 119

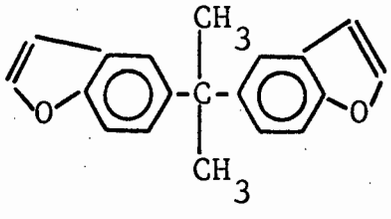
The alternative process:



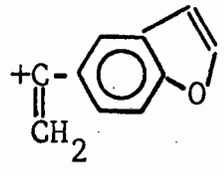
mass 143

also occurs but not to the same extent as the former process. In the spectrum, the peak at mass 143 is small. The ions produced in both processes are stabilised by resonance with the aromatic nuclei. The former may rearrange to a hydroxytropylium ion to stabilise. If this is the case then the reason for the predominance of the former process is clear.

(ii) 2,2-bis-(benzofur-5-yl)propane:



The mass spectrum of the sample collected from the chromatograph showed that two impurities were present. The peaks at 276 (M^{+}), 261$(M-CH_3)^{+}$ and 143

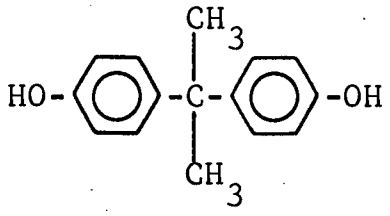


are expected for this compound and

are formed by processes which have been detailed in section D.II.5.d.i. above.

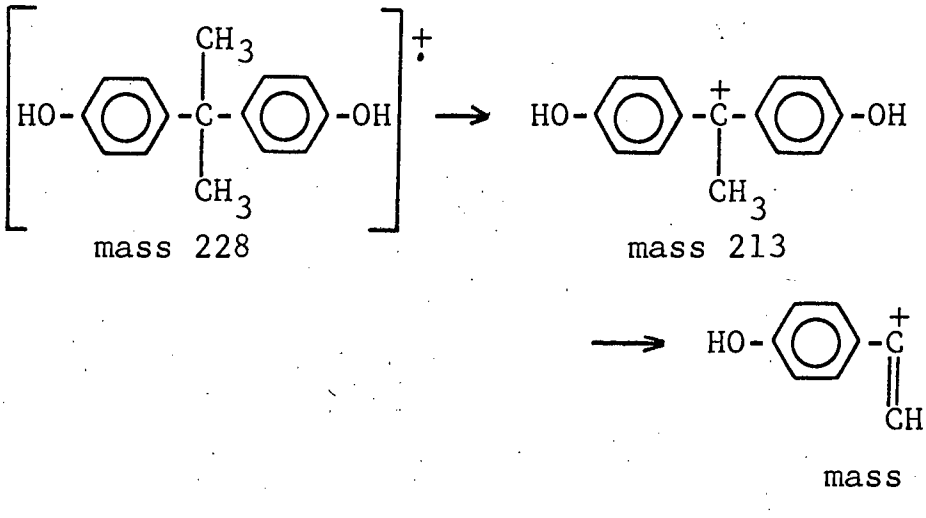
In addition to these peaks, peaks of masses 266, 252, 251 and 237 appear. The peaks of mass 252 and 237 arise from the presence of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane in the sample (section E.II.4.m.). The peaks at $\frac{m}{e}$ 266 (M^{+}) and $\frac{m}{e}$ 251 $(M-CH_3)^{+}$ are probably due to the presence of 2-(1,4-benzopyran-6-yl)-2-(p-hydroxyphenyl)propane (section E.II.4.m.).

(iii) Bisphenol A:

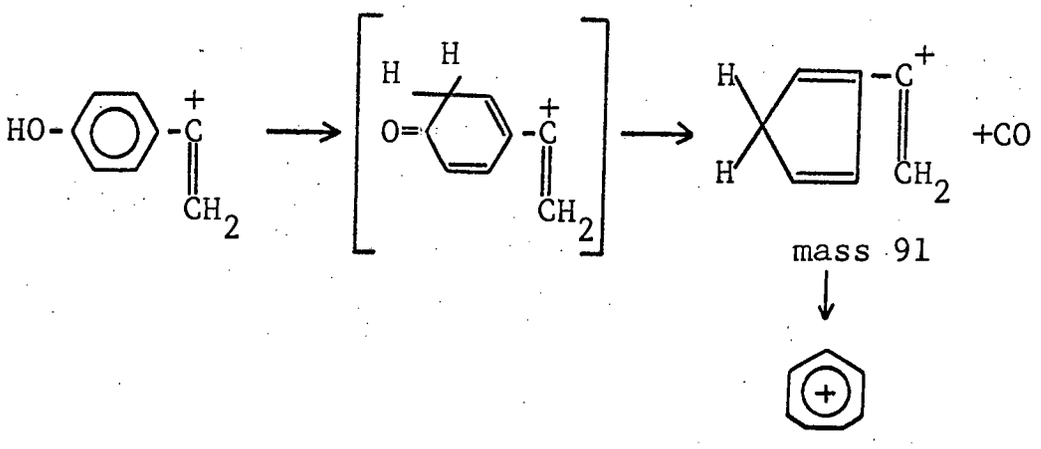


The mass spectrum shows four major peaks - the base peak of mass 213, the molecular ion peak of mass 228, a peak of mass 119, and a small peak of mass 91.

The processes which occur to give the first three ions are analogous to those which occur with 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane and are summarised:



The small peak of mass 91 evidently arises from loss of CO from the last ion:



D.II.5.e: Elemental analyses

Elemental analyses of the starting products viz. the diglycidylether of Bisphenol A and p,p'-diamino-diphenylmethane and of the synthetic compounds are collected in table 3.

Table 3:

Compound		%C	%H	%N	%Cl
Benzofuran:	obtained	81.0	5.3	-	-
	theoretical	81.4	5.1	-	-
2-(benzofur-5-yl)-2-(p-hydroxy phenyl) propane	obtained	78.4	6.3	-	-
	theoretical	80.9	6.3	-	-
p,p'-diamino-diphenylmethane	obtained	78.1, 78.5	7.15, 7.00	14.16, 14.52	-
	theoretical	78.7	7.11	14.33	-
diglycidyl ether of Bisphenol A	obtained	73.76, 73.92	7.22, 7.00	-	0.38 0.61 0.46 0.30
	theoretical	74.08	7.105	-	-
p-isopropenyl-phenol	obtained	80.3	7.4	-	-
	theoretical	80.6	7.4	-	-

Table 4: Thin-layer chromatography data:

Compound	Eluent (v/v)	R_F value	Colour of Spot		
			Untreated	I_2 vapour	H_2SO_4 / Heat
benzofuran	Petroleum ether B.Pt.60-80°C	0.70	-	yellow	scarlet
2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane	Methanol 7 Chloroform 93	0.41	-	yellow	reddish-brown
Bisphenol A	Methanol 15 Chloroform 85	0.72	-	yellow	reddish-brown
p-isopropenylphenol	Methanol 18 Chloroform 90	0.82	-	white surrounded by yellow	ochre-brown
p-isopropylphenol	Methanol 7 Chloroform 87	0.63	-	yellow	light-brown
N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane	Methanol 7 Chloroform 93	0.59	-	navy blue	-
acetaldehyde 2,4-dinitrophenylhydrazone	Petroleum ether B.Pt.60-80°C	0.40	yellow	-	-

D.II.5.f: Thin-layer chromatography

Thin-layer chromatography was particularly useful for determining the purity of synthetic compounds and also in providing confirmation of the identification of reaction products by the comparison of R_F values of standard chemicals and unknowns. In all cases glass plates 3" long by 1½" wide coated with a 0.25 mm. thick layer of silica gel (Merck* silica gel C grain size 10-40μ with 10% calcium sulphate binder) were used. The plates were spotted with a solution of the compound in question from a finely drawn capillary. After evaporation of the solvent the compound was eluted by the submersion of the end of the plate in a suitable eluent in a closed container. Two methods of marking were used, namely the action of iodine vapour and the action of heat after spraying the plate with 2N sulphuric acid.

The synthetic 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane was finally purified by thin-layer chromatography (section E.II.1.c.).

Data are collected in table 4.

*Trade name

D.II.5.g: Melting points and boiling points

The melting points and boiling points of the more uncommon compounds are collected in Table 5.

Table 5:

Compound	M.Pt.(°C)	B.Pt.(°C)	Ref.
benzofuran	-	174	27
2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane	101-103	-	-
2,2-bis-(benzofur-5-yl) propane	80-81	-	-
Bisphenol A	155	-	27
ethyl o-formylphenoxy acetate	47-48	-	7
o-formylphenoxyacetic acid	132	-	7
2-(p-hydroxyphenyl) propan-2-ol	102-104	-	-
p-isopropenylphenol	83-84	-	14
p-isopropenylphenyl benzoate	110	-	-
p-isopropylphenol	62.6	-	27
p-isopropylphenyl benzoate	72-73	-	9
N,N,N',N'-tetramethyl-p,p'-diaminodiphenyl-methane	91-92	-	27

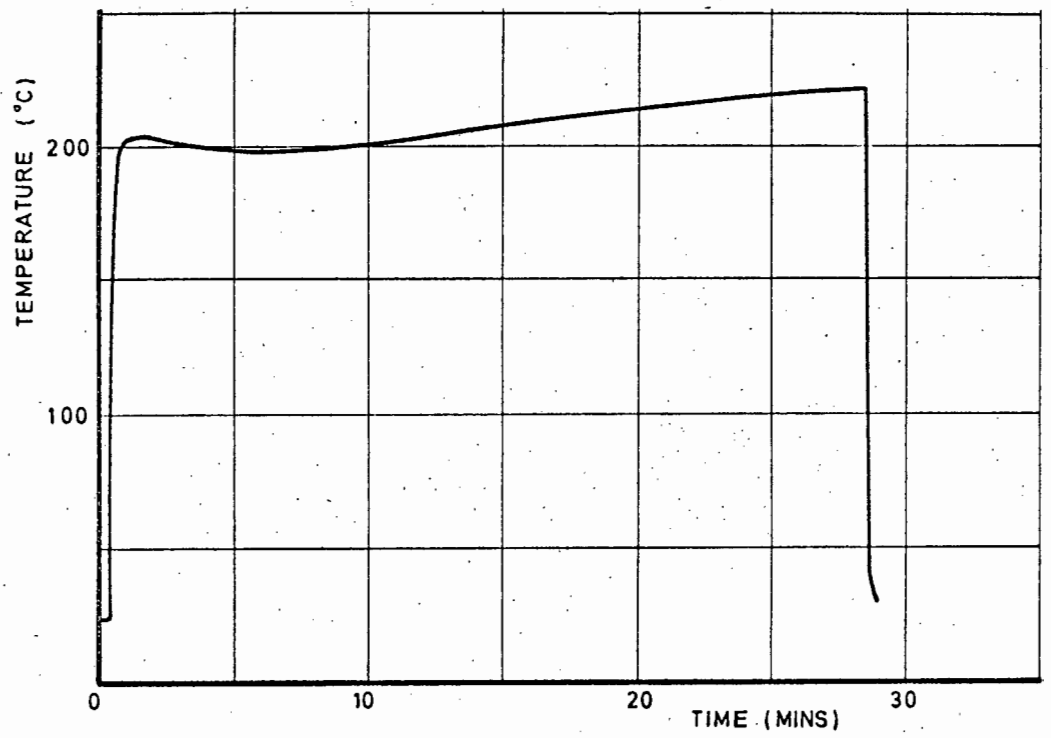


Figure 16: EXPERIMENT II

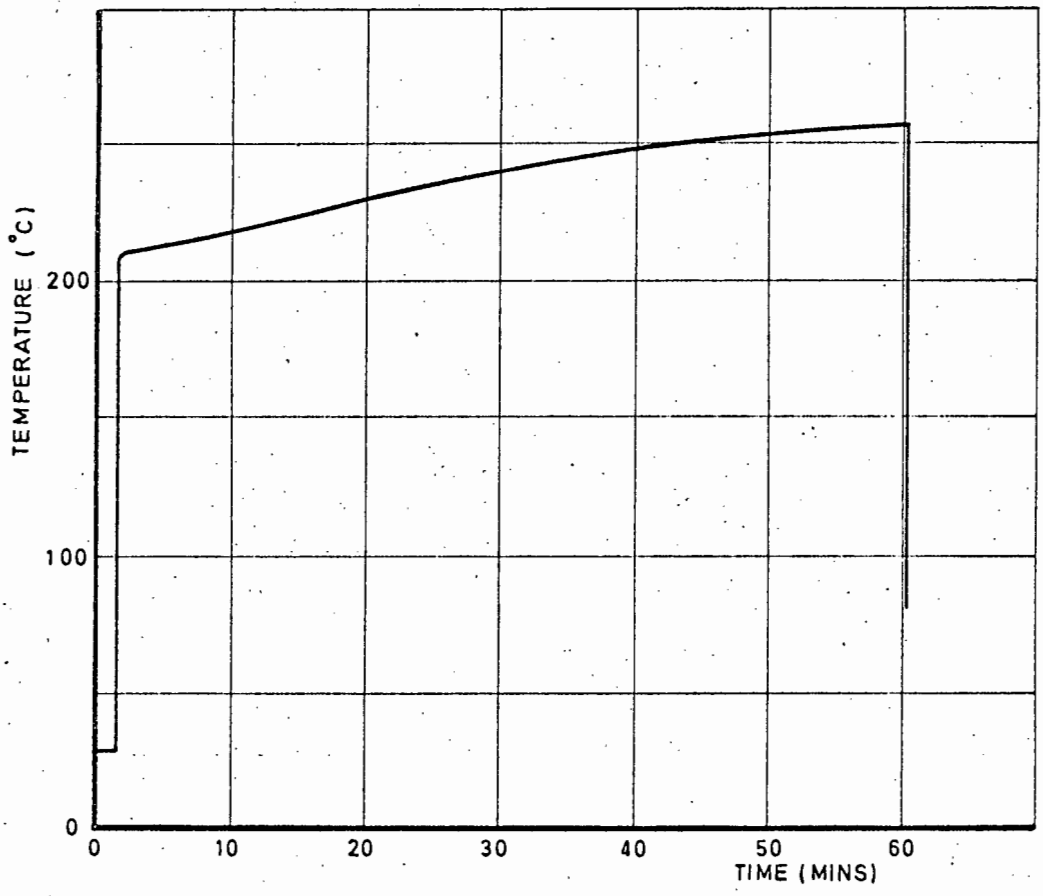


Figure 17: EXPERIMENT III

E. Part I: Experimental Results

E.I.1: Post-cure/degradation details

In all the experiments, the resin discs were cured for 20 hours at 95°C in airtight polythene moulds.

Experiment I.

(i) After the 95°C cure the discs were post cured in air at 130°C for 16½ hours.

(ii) The discs retained their transparency and honey colour.

Experiment II.

(i) Discs cured at 95°C were post-cured at an initial pressure of 0.7 mm. of mercury in the apparatus described in section D.I.3. The temperature-time history is given in figure 16.

(ii) No colour change followed the heat treatment.

(iii) The discs suffered no weight loss.

Experiment III.

(i) Discs cured at 95°C were post-cured/degraded at an initial pressure of 0.7 mm. of mercury in the apparatus described in section D.I.3. The temperature-time history is given in figure 17.

(ii) No colour change followed the heat treatment.

(iii) Weight losses of 0.0628% and 0.0627% were recorded for the two discs.

Experiment IV.

(i) Discs cured at 95°C were post-cured/degraded at an initial pressure of 0.5 mm. of mercury in the apparatus described in section D.I.3. The temperature-time history is given in figure 18.

(ii) The discs emerged from the heat treatment the same honey colour as before.

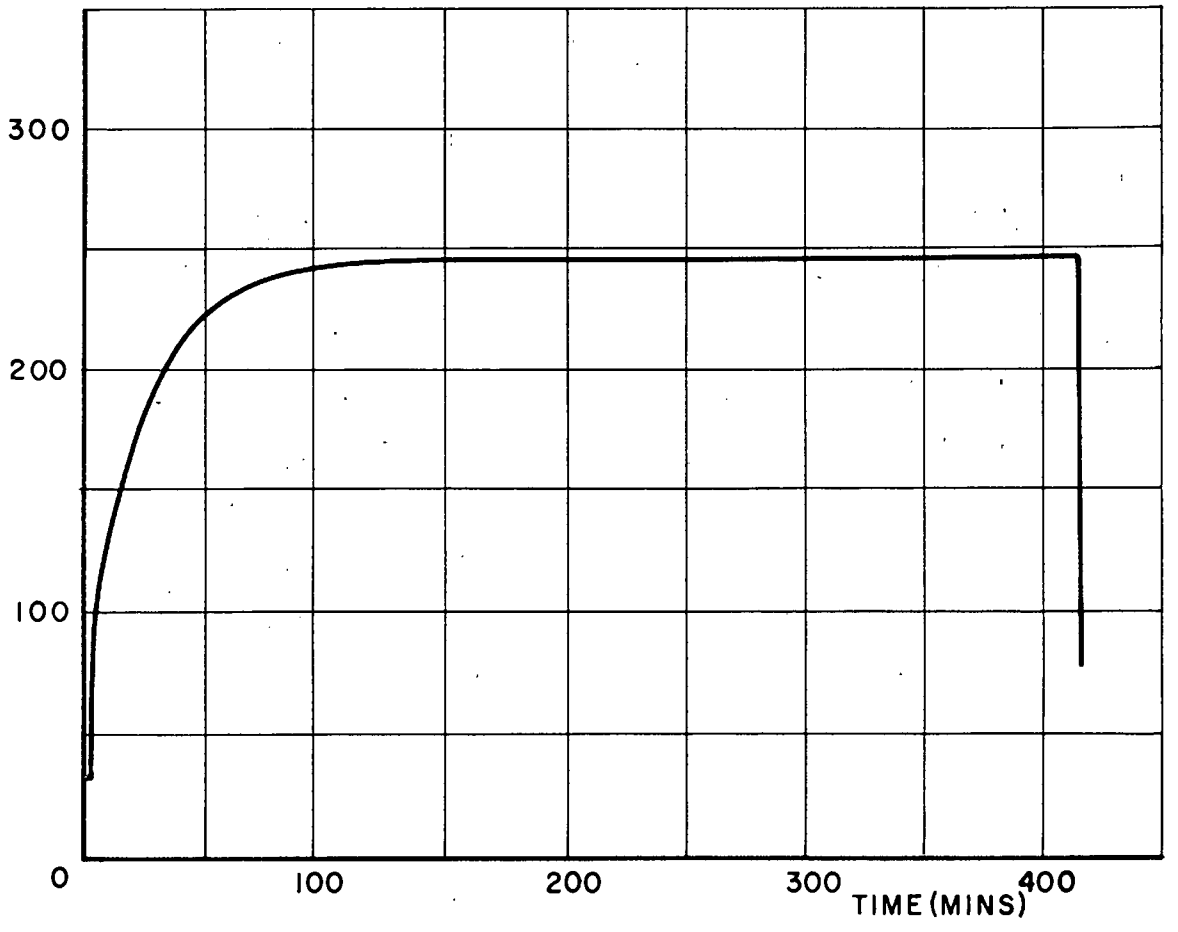


FIGURE 18: EXPERIMENT IV

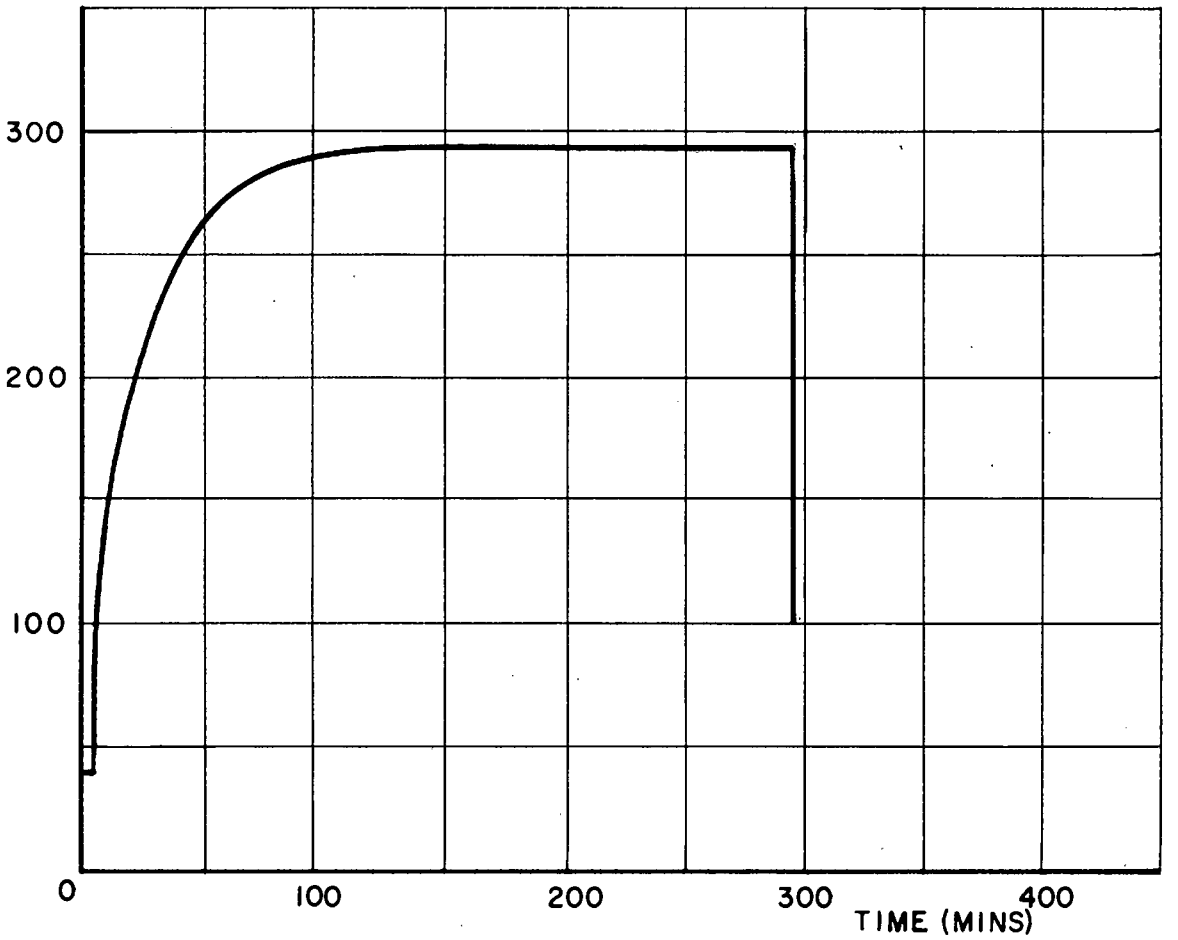


FIGURE 18 A: EXPERIMENT V

(iii) Weight losses of 0.262% and 0.194% were recorded for the two discs.

Experiment V.

(i) Discs cured at 95°C were post-cured/degraded at an initial pressure of 0.7 mm. of mercury in the apparatus described in section D.I.3. The temperature-time history is given in figure 18A.

(ii) The discs emerged from the heat treatment darkened in colour and the darkening was uniform throughout the discs.

(iii) Weight losses of 7.8% and 4.9% were recorded for the two discs.

E.I.2: Results of dielectric measurements

E.I.2.a: Accuracy of dielectric measurements

A preliminary experiment to test the reproducibility of results was carried out on a disc of cured epoxide resin. The results showed that where values of the loss tangent were of the order of 10^{-2}, values could be quoted to 0.5×10^{-3} i.e. a spread of 10^{-3}. The source of greatest uncertainty appeared to be the readings of frequency on the oscillator. Values of ϵ are accurate to two decimal places.

Except for Experiment I results for loss tangent and dielectric constant are tabulated, values for various temperatures at a fixed frequency being grouped together; the results are plotted in concise form as contour diagrams. The discs of resin used in Experiment I, which were cured at 130^{o}C proved unstable when measurements at temperatures near the cure temperature were attempted. This point is taken up in the Discussion (section F). The full results are, therefore, not given for these discs; only values at a frequency of 1.05 kc/s will be tabulated for the sake of the Discussion.

E.I.2.b: Dielectric results in tabular form (see Appendix A)

Notes on dielectric results

(1) In all four experiments (Experiments II, III, IV and V) the effect of leaving a disc of the resin at a temperature greater than 100^{o} was a lowering of the value of the dielectric constant ϵ without any significant change in tan δ values. The same effect occurred when discs were heated to temperatures above

100°, cooled and then reheated. In making dielectric measurements the discs had to be left at elevated temperatures for appreciable times (some hours) and since the measurements extended over a period of days the discs were usually cooled and left at room temperature overnight.

The effect can be seen in Experiment II in the region of 160°C, in Experiment III at all temperatures above 100°C, in Experiment IV at all temperatures above 100°C and particularly around 160°C, and in Experiment V in the region of 160°C. In Experiments III and IV, the effect was such that the normal rise with temperature of ϵ , which should have accompanied the rapid rise with temperature of tan δ was not noted except at the lowest frequencies.

There appeared no way of obviating this effect which was characteristic of the resin. The result is that values of ϵ at the higher temperatures are not simply related to those at lower temperatures and in fact may not have any quantitative significance.

(2) As will be shown fully in the Discussion (section F) values of tan δ and ϵ at temperatures in the region of 220°C and above are time dependent. The reported values of tan δ and ϵ at these temperatures have only qualitative significance.

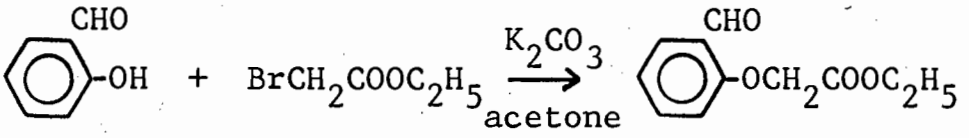
E. Part II: Experimental Results

E.II.1: Synthetic methods

E.II.1.a: Benzofuran

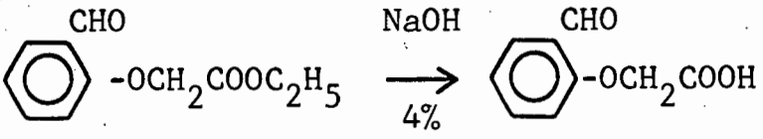
The synthesis of benzofuran was based upon a method of Foster and Robertson.[26] Condensation of salicylaldehyde with bromoacetic ester yielded ethyl o-formylphenoxy acetate. This ester was hydrolysed to o-formylphenoxy acetic acid. The last stage involved cyclisation of the acid to form benzofuran-2-carboxylic acid and benzofuran. The yield of benzofuran from the last reaction was 8.5%.

E.II.1.a.i: Ethyl o-formylphenoxy acetate



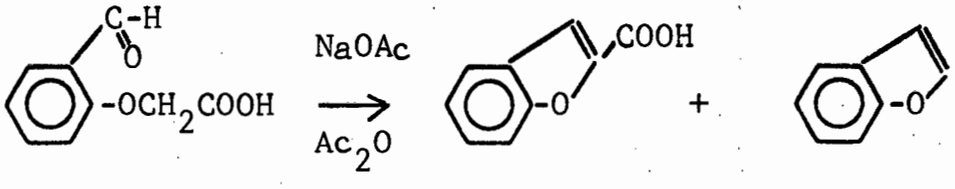
28 g. of salicylaldehyde was refluxed with 25.4 mls. of bromoacetic ester, 46 g. of anhydrous potassium carbonate and 350 mls. of anhydrous acetone for 1½ hours. The solution was cooled and filtered. The filtered potassium carbonate and bromide were washed well with acetone and the washings added to the filtrate. The acetone solution was poured into 2 litres of water and stirred. The ethyl o-formylphenoxy acetate crystallised and was filtered from the solution. 42.5 g. of the ester was recovered. The crude product was recrystallised from ethyl acetate to yield a white crystalline product melting at 45-46°C. (Lit., 47-48°C).

E.II.1.a.ii: o-Formylphenoxy acetic acid



42.5 g. of the ester was shaken with 1050 mls. of 4% sodium hydroxide solution in the cold until complete solution of the ester had occurred. The solution was treated with 400 g. of ammonium chloride and 1:1 hydrochloric acid until the pH of the solution was 2. The precipitated acid was filtered from the solution and washed with a small quantity of water. The acid was dissolved in 800 mls. of tetrahydrofuran and the resulting solution was dried over anhydrous sodium sulphate. The filtered solution was distilled to reduce the quantity of solvent to approximately 1/5 of its original volume and the acid crystallised from this solution. 30 g. of a pale yellow crystalline solid melting at 134°C was recovered (lit., 132°C).

E.II.1.a.iii: Benzofuran



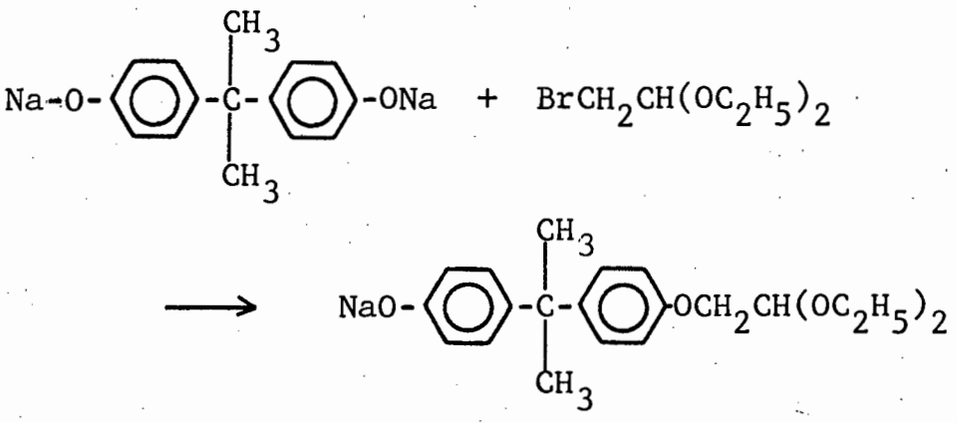
30 g. of o-formylphenoxy acetic acid was refluxed for 45 minutes with 300 mls. acetic anhydride containing 84 g. anhydrous sodium acetate. The solution was cooled and poured into 800 mls. water. A solution of 60 g. sodium hydroxide in 300 mls. water was added till the pH of the solution was 7.5. This solution was shaken with two 100 ml. portions of diethylether. The combined ether extracts were dried over anhydrous sodium sulphate, filtered and distilled. A colourless liquid

(2.2 g.) boiling between 167°C and 171°C, was collected. The product, benzofuran, was redistilled, boiling point 173°C. Elemental analyses are given in Table 3.

E.II.1.b: 2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)propane

The method chosen for the synthesis of this compound followed a method for the synthesis of benzofuran which involves cyclisation of the intermediate phenoxyacetaldehyde diethyl acetal (Stoermer[59]). The yields of the cyclisation reaction are extremely low because the catalysts employed (zinc chloride, sulphuric acid) cause extensive polymerisation of the resulting structure. The method was chosen, however, because of the availability of Bisphenol A and the difficulties involved in the preparation of suitable intermediates which would have been required for the synthesis if the method described for the preparation of benzofuran (section E.II.1.a.) were to have been used. The initial condensation of bromoacetal with Bisphenol A does not occur readily. Various solvents were tried, the most successful being dimethyl sulphoxide.

E.II.1.b.i: Bisphenol A 2,2-diethoxyethyl ether

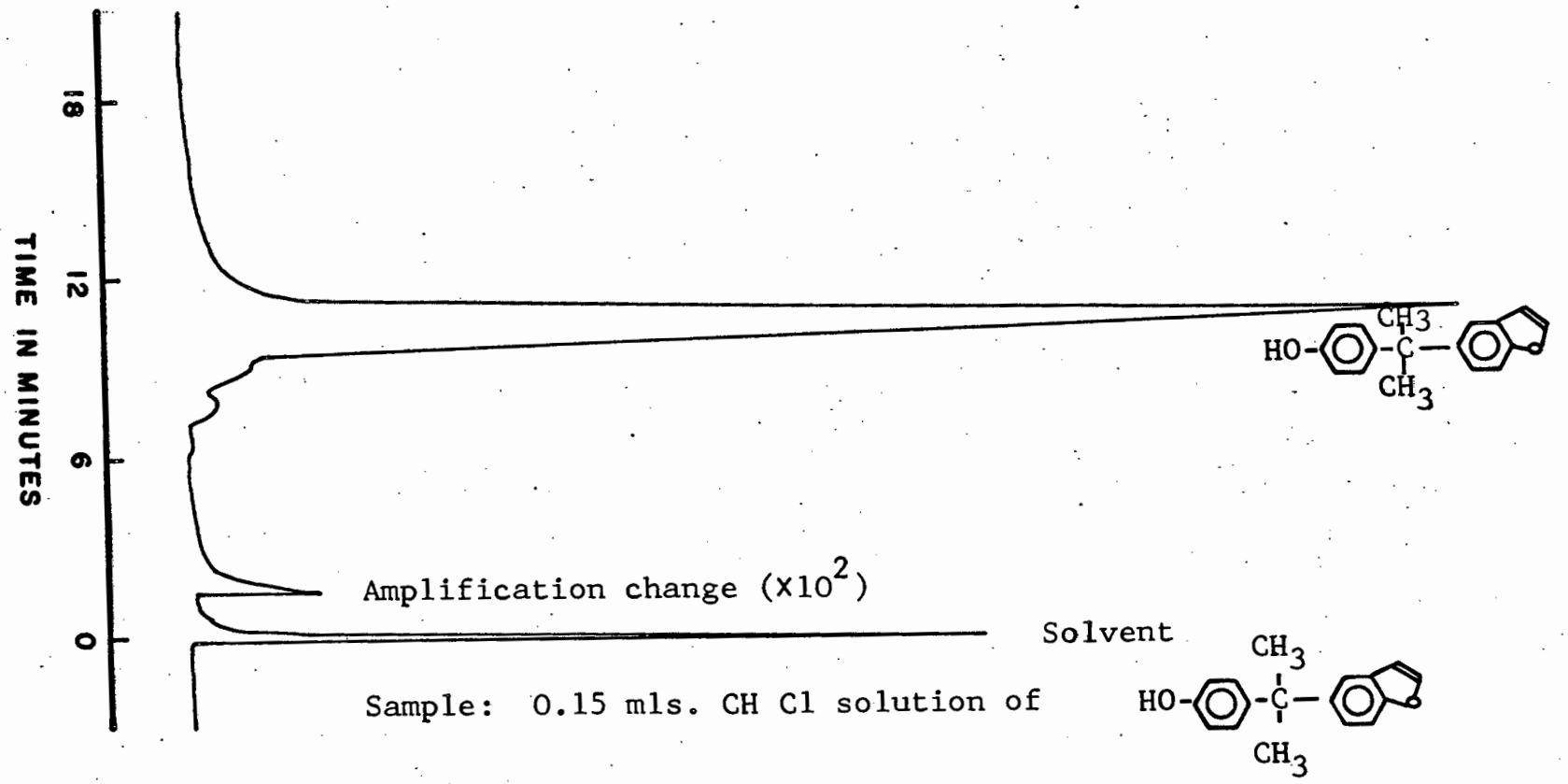


34.6 g. (2 mols.) of sodium was dissolved in 510 mls. of dry ethanol. 170.7 g. (1 mol.) of

Bisphenol A was dissolved in this solution. The ethanol was distilled off on a water bath and finally under vacuum to yield a cake of the disodium salt of Bisphenol A. The disodium salt was dissolved in 500 mls. of dimethyl sulphoxide. 170.7 g. (1 mol.) of bromoacetal was added and the solution was refluxed for 10½ hours. At the end of this period the solution was cooled and poured into 3 litres of water and stirred. Two 200 mls. portions of diethylether were used to extract the product from the aqueous solution. The combined ether extracts were washed once with 100 mls. of 1:3 hydrochloric acid and with four 100 mls. portions of water. The ethereal solution was dried over anhydrous sodium sulphate and distilled. After removal of the solvent the remaining liquid was distilled at reduced pressure. A fraction boiling between 294°C and 306°C at a pressure of 2.5 cms. of mercury was collected. 166.3 g. of a pale green fairly viscous liquid was collected. This was a mixture containing predominantly the 2,2-diethoxyethyl ether of Bisphenol A together with quantities of Bisphenol A and smaller quantities of the disubstituted product. No attempt was made at this stage to separate the mixture. An infra-red spectrum of the mixture is shown in Appendix B.

E.II.1.b.ii: 2-(Benzofur-5-yl)-2-(p-hydroxyphenyl) propane

42.2 g. of the product from the previous reaction was refluxed for 5 minutes with 30 mls. of 30% sulphuric acid. The mixture was cooled and shaken with 100 mls. of chloroform. The chloroform extract was dried over anhydrous sodium sulphate and distilled. After removal of the solvent the remaining liquid was distilled at reduced pressure. A fraction boiling at 280°C at a



Sample: 0.15 mls. CH Cl solution of HO-C(CH$_3$)$_2$-

Column: 7'x ⅜" diam. glass — 15% E30 — 60 - 72 mesh silanised Celite.

Temperature: 243°C.

Carrier: Nitrogen.

Flow Rate: 171 mls./min.

Figure 19.

pressure of 2.5 cms. of mercury was collected. A large residue of tarry products remained in the flask. The distillate was dissolved in 15 mls. of chloroform. From the solution Bisphenol A (2.5 g.) which is not very soluble in chloroform, crystallised and was filtered off. The filtrate containing the required product was chromatographed. A 7 feet x $\frac{3}{8}$" diameter glass preparative column containing 15% E30 methyl silicone gum operating at 243°C was employed. The chromatogram is shown in figure 19. The chromatogram showed that the 2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane contained small quantities of two impurities. The 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane was collected from the column as a substantially pure, white crystalline product (0.3 g.). The inherent yield of the reaction is, in fact, higher than this figure would suggest since it reflects the efficiency of the collection from the chromatograph column which was in the region of 20%. An infra-red spectrum of the product is shown in Appendix B.

The purity of the product was investigated by thin-layer chromatography. The results showed that the product still contained quantities of impurities. In an effort to remove these, 18 mg. of the product was chromatographed on a thin-layer plate of dimensions 8" x 4" covered with a 1 mm. thick layer of silica gel. (section D.II.5.f.). The eluent employed was a mixture of 5 parts methanol and 95 parts chloroform (v/v). A chloroform solution of the product was introduced from a capillary onto the plate along a horizontal line. After elution and evaporation of eluent from the plate, the eluted sample was marked by spraying with water. The portion of the plate

covered by the required product was marked. The plate was dried and the required portion of silica gel scraped off the glass plate. The purified product was dissolved off the silica gel in chloroform. Evaporation of the chloroform yielded the crystalline product (8 mg.). The infra-red spectrum of the product showed no change so that the original product could not have contained large quantities of impurities. The purified product melted completely at 103°C. Preliminary melting occurred in the range 99-101°C. The degradation product which thin-layer chromatography showed to be a pure sample of the same compound showed similar behaviour around its melting point (104°C), preliminary melting occurring in the range 101-103°C.

The purity of the purified product was checked again by thin layer chromatography. The results showed the presence of a small quantity of impurity. Further efforts to improve the purity of the sample were not made firstly because the percentage of impurity was very small and secondly because large quantities of a purer product were available from the separation of the degradation products. The purpose of the synthesis was the confirmation of the structure of the corresponding degradation product. The purity of the synthetic product was more than sufficient for this purpose.

The accurate mass of the molecular ion ($\frac{m}{e}$ 252) in the product's mass spectrum was 252.117413 (theor: 252.115023). In section G a possible synthesis of compounds containing the benzofuran nucleus will be outlined.

The compound 2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane has not been previously reported in the literature.

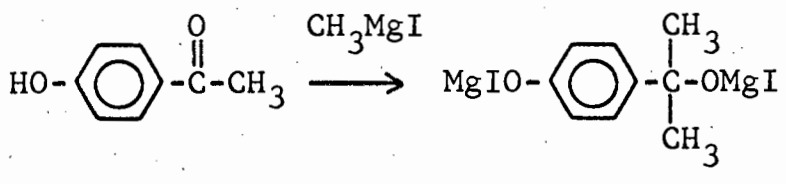
E.II.1.c: p-Isopropenylphenol

The synthesis of p-isopropenylphenol has been reported previously only once in the literature. Corson et al.[14] synthesised the compound by the dehydrogenation of p-isopropylphenol and also by the thermal and catalytic cracking of Bisphenol A and its diacetate.

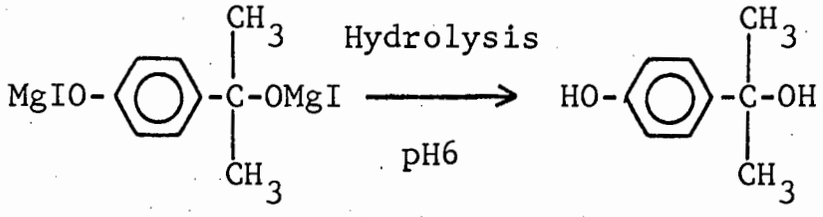
A novel synthesis of the compound is described below. The method involves the synthesis of 2-(p-hydroxyphenyl)propan-2-ol which, when passed through a gas chromatograph column under the right conditions, loses water to yield p-isopropenylphenol together with other condensation products. The method is very convenient since the dehydration of the intermediate carbinol and the separation of the resulting p-isopropenylphenol from other products are accomplished in one step. The p-isopropenylphenol is collected from the column as a pure crystalline compound. The disadvantage of the method is that the quantity of the product collected is dependent on the capacity of the column. Using the column described, quantities in the region of hundreds of milligrams were collected by repeated injections of the intermediate. There is no reason, however, why the scale of the operation could not be increased by the use of suitably large columns. The preparation of the intermediate is straightforward.

E.II.1.c.i: 2-(p-hydroxyphenyl)propan-2-ol

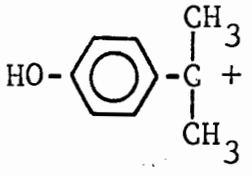
The synthesis involves the intermediate formation of a Grignard complex from p-hydroxyacetophenone.



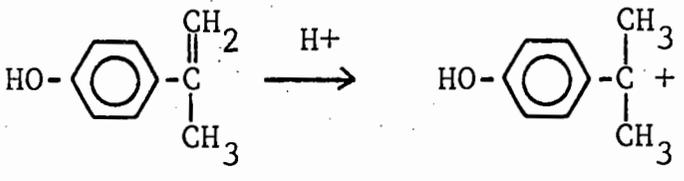
followed by hydrolysis of the complex with ammonium chloride solution and acidification of the solution to pH6:



The final pH is critical. Slightly acid conditions are necessary to liberate the phenolic hydroxyl group. The 2-(p-hydroxyphenyl)propan-2-ol is, however, particularly susceptible to acid-catalysed polymerisation through the formation of the carbonium ion:



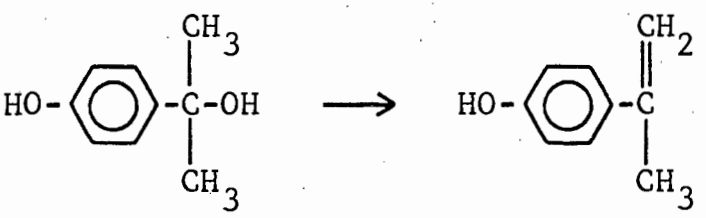
This carbonium ion is stabilised by the presence of the electronegative hydroxyl group para to the isopropyl group which tends to increase the electron density of the aromatic ring. p-Isopropenylphenol is similarly succeptible to cationic polymerisation through the formation of the same carbonium ion:



1.96 g. of magnesium turnings was dissolved in a solution of 5 mls. of iodomethane in 50 mls. of anhydrous diethylether. The solution was refluxed for 15 minutes to complete the reaction. A solution of 5 g. of p-hydroxyacetophenone in 90 mls. of diethyl-ether was added slowly with shaking. When the

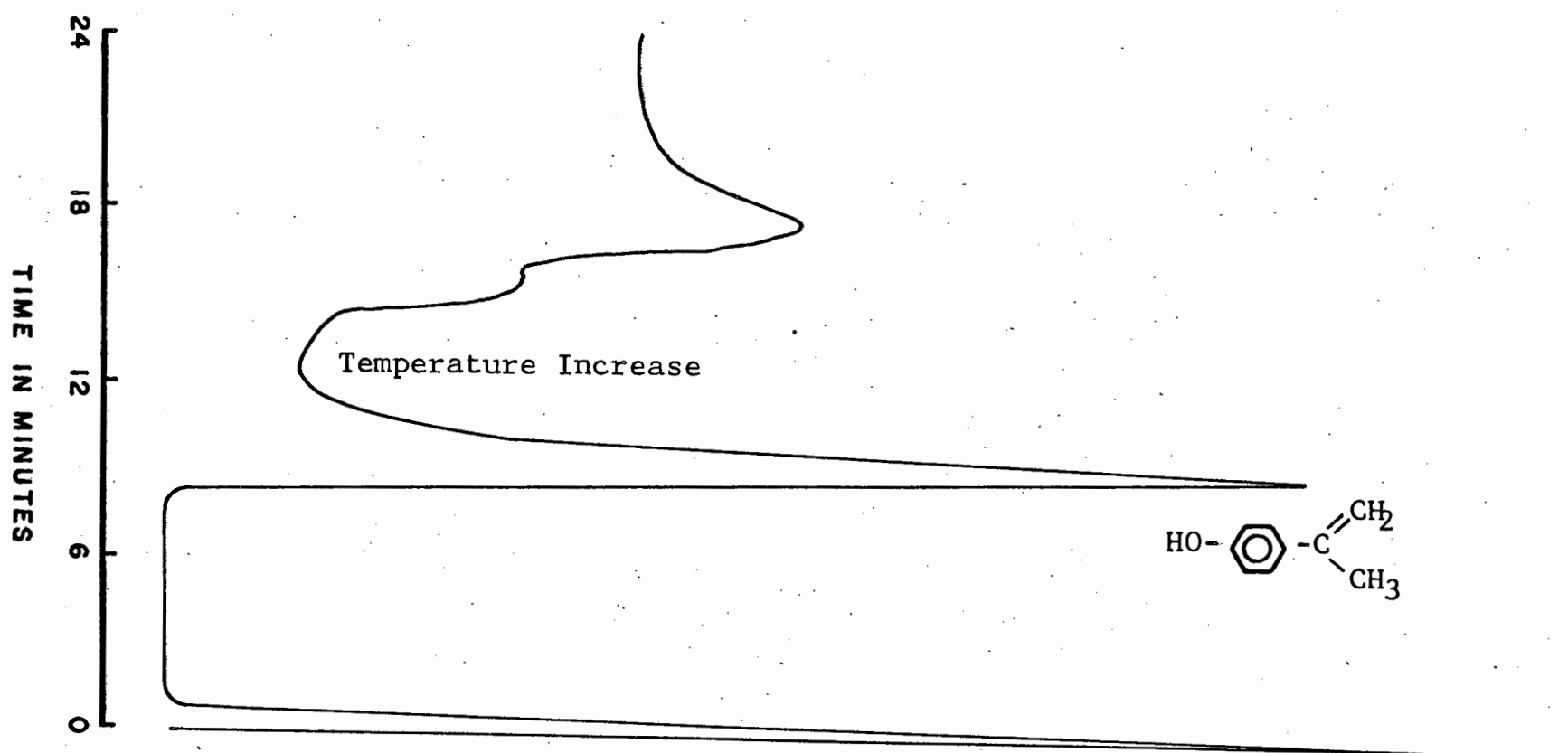
addition was complete the mixture was refluxed for 15 minutes to complete the reaction. The Grignard complex is an off-white crystalline substance very insoluble in ether. 100 mls. of 10% ammonium chloride solution was added to decompose the complex. The resulting solution was titrated with 10% hydrochloric acid to pH6. The ethereal layer was separated from the aqueous layer, the latter being washed with a further portion of 50 mls. of ether. The combined ether extracts were dried over anhydrous sodium sulphate, filtered and distilled to reduce the bulk of the solution. The 2-(p-hydroxyphenyl)propan-2-ol crystallised from this solution and was filtered. The yield was 4.5 g. of a white crystalline solid which turned slightly pink on exposure to air. The crude product was recrystallised from a solution in equal volumes of chloroform and ether to yield white crystals melting at 102-104°C.

E.II.1.c.ii: p-Isopropenylphenol



An ethereal solution of 2-(p-hydroxyphenyl) propan-2-ol was chromatographed. A 7 feet long, ⅜" diameter glass preparative column containing 25% E30 methyl silicone gum on 60 - 72 mesh Celite* operating at 166°C was used. After the appearance of the p-isopropenylphenol peak the operating temperature was increased at a rate of 24°C/min. to

*Trade name



Sample: 0.2 mls. ether solution of HO- -C-OH (CH_3, CH_3)

Column: 7' x ⅜" diam. glass — 25% E30 — 60 - 72 mesh silanised Celite.

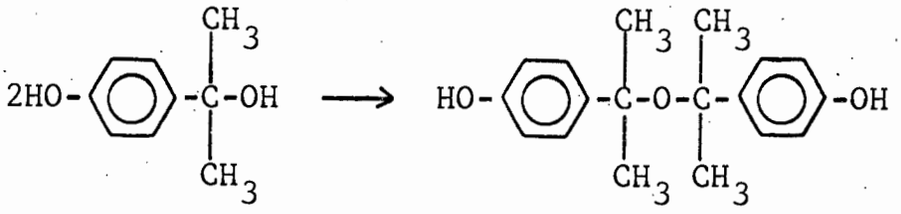
Temperature programme: 166°C increased at 12 mins. at rate of 24°C/min. to 235°C.

Carrier: Nitrogen.

Flow Rate: 187 mls./min.

Figure 20.

235°C in order to remove two higher molecular weight compounds which were also produced in small quantities. The nature of these compounds was not investigated but they were probably condensation products produced by the elimination of water from two hydroxyl groups to produce ether structures e.g.



The chromatogram is shown in figure 20.

From 0.8 g. of the starting product 0.25 g. of p-isopropenylphenol was collected by repeated injections. This figure, however, reflects the efficiency of the collection device. During the collection, the compound collected in the trap either as white crystals deposited directly from the vapour or as very pale yellow crystals formed from condensation of the vapour to a melt which then crystallised. The melting point of both forms was identical, namely 81 - 83°C. Corson et al.[14] report a corrected melting point of 83-84°C. An infra-red spectrum of the compound is shown in Appendix B. p-Isopropenylphenyl benzoate was prepared from the phenol by the normal Schotten-Baumann method (m.p. 110°C). An infra-red spectrum of the substance is shown in Appendix B and a nuclear magnetic resonance spectrum in Appendix C. Elemental analyses are given in Table 3.

It is possible that this method of dehydration of carbinols may have wide application. It may be particularly useful where dehydration under acid conditions yields a carbonium ion which is likely to cause polymerisation rather than dehydration.

E.II.2: Degradation data

E.II.2.a: Experiment I

(i) Initial weight of resin: 15.1294 g.

(ii) The resin was in the form of small bars (section D.II.2).

(iii) The resin was evacuated for 5½ hours before degradation. A final pressure of 10^{-6} mm. of mercury was recorded.

(iv)	Time of degradation :	150 minutes.
	Final isothermal degradation temperature :	303.7°C
(v)	Final weight of resin :	11.5403 g.
	Percentage weight loss :	23.7%
	Percentage linear shrinkage :	3%

(vi) The resin bars after degradation were a uniform dark red-brown colour. Shrinkage occurred but the bars were not appreciably distorted.

(vii) No reaction products collected in the portion of the reaction vessel covered by the heater. A small quantity collected in the portion of the reaction vessel not covered by the heater. Large quantities collected in the fore-tube. All these products were dissolved off the apparatus in chloroform (section D.II.4) to a total volume of solution of 100 mls.

(viii) Products which had collected in the trap maintained at a temperature of -12.2°C during the degradation were dissolved in dry methanol to a total volume of solution of 100 mls. (section D.II.4) and the solution was reserved for analysis.

(ix) Products collected in the trap maintained at a temperature of -77°C during the degradation were dissolved in dry methanol to a total volume of solution of 25 mls. (section D.II.4) and the solution was reserved for analysis. The solution was stored at a temperature of 0°C.

(x) Products collected in the trap maintained at a temperature of -196°C were reserved for analysis (section D.II.4).

E.II.2.b: Experiment II

(i) Initial weight of resin : 18.32245 g.

(ii) The resin was in the form of small bars (section D.II.2).

(iii) The resin was evacuated for 5½ hours before degradation. A final pressure of 10^{-5} mm. of mercury was recorded.

(iv)	Time of degradation :	150 min.
	Final isothermal degradation temperature :	304°C
(v)	Final weight of resin :	13.25525 g.
	Percentage weight loss :	27.6%
	Percentage linear shrinkage :	3%

(vi) The resin bars after degradation were a uniform dark red-brown colour. Shrinkage occurred but the bars were not appreciably distorted.

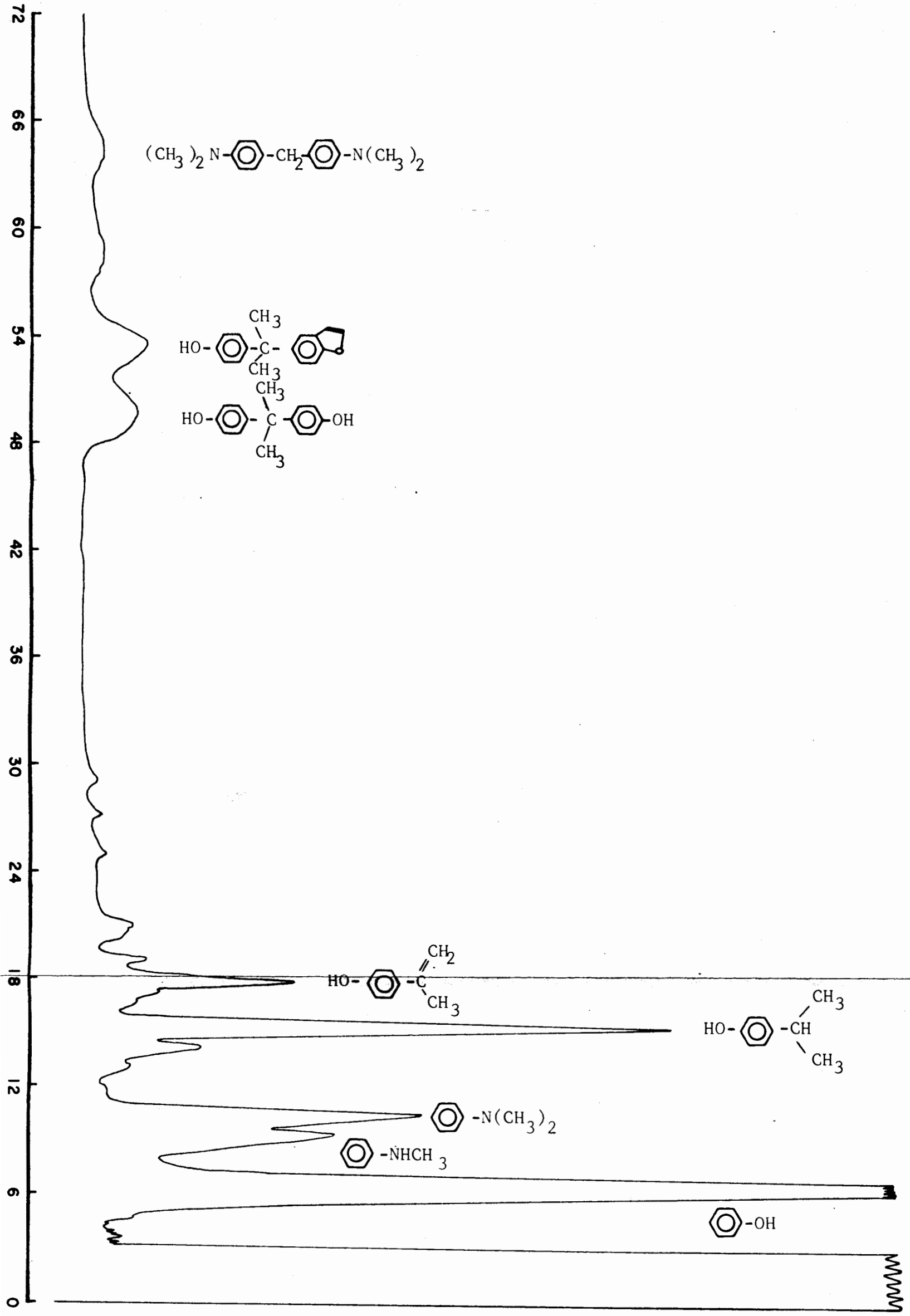
(vii) No reaction products collected in the portion of the reaction vessel covered by the heater. A small quantity collected in the portion of the reaction vessel not covered by the heater. Large quantities collected in the fore-tube. All these products were dissolved off the apparatus in diethylether. (section

D.II.4).

(viii) Products which had collected in the trap maintained at a temperature of -12.2°C during degradation were dissolved in diethylether. (section D.II.4). The ethereal solutions of the degradation products from the reaction vessel the fore-tube and this trap were combined to a total volume of solution of 100 mls. and the solution was reserved for analysis.

(ix) Products collected in the trap maintained at a temperature of -77°C during the degradation were dissolved in diethylether. Water, which is the major component of the degradation products in this trap was separated from the ethereal solution. The ethereal solution of total volume 25 mls. was reserved for analysis.

(x) Products collected in the trap maintained at a temperature of -196°C during degradation were reserved for analysis (section D.II.4).



Sample: 0.5 mls. solution of products from -12.2°C trap - Experiment I.

Column: 7'X ⅜" diam. glass — 25% E30 — 60 - 72 mesh silanised Celite.

Temperature Programme: 131°C increased at 10½ mins. at rate of 6°C/min. to 230°C.

Carrier: Nitrogen.

Flow Rate: 231 mls./min.

Figure 21.

E.II.3: Degradation products

E.II.3.a: Experiment I

E.II.3.a.i: Products in -12.2°C trap

The methanol solution of the products from this trap was initially slightly cloudy. A very small quantity of precipitated matter settled onto the bottom of the flask. The clear solution was chromatographed on a 7 feet long by ⅜" diameter glass preparative column containing 25% E30* methyl silicone gum on 60 - 72 mesh silanised Celite*. The initial temperature of 131°C was increased 10½ minutes after injection at a rate of 6 °C/minute to 230°C. A chromatogram of the separation is shown in figure 21. Fractions corresponding with individual peaks were collected from repeated injections of the solution. Phenol, N-methylaniline, N,N-dimethylaniline, p-isopropylphenol, p-isopropenylphenol, Bisphenol A and 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane were identified (section E.II.4). The presence of N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane was suspected but a conclusive identification was not obtained. The percentage of water in this solution was determined. (section E.II.4.a).

E.II.3.a.ii: Products from reaction vessel and fore-tube

The chloroform solution of these products showed extensive precipitation. The clear solution was chromatographed. The chromatogram was similar to that of the products from the -12.2°C trap, larger quantities of the higher molecular weight components being present.

*Trade name

Because of the extensive precipitation which had occurred and which may have indicated some degradation in the solution, further analyses were not made. Chloroform was evidently not an ideal solvent for these products and was replaced by diethylether in Experiment II.

E.II.3.a.iii: Products in -77°C Trap

The percentage of water in the methanol solution of products in this trap was determined (section E.II.4.a).

After the water determination the methanol solution was dried over anhydrous sodium sulphate. The filtered solution was chromatographed on a 15 ft. long by ⅜" diameter glass column containing 25% PEG 20M*, polyethylene glycol on 60 - 72 mesh silanised Celite*. Repeated injections over a period of a few hours showed wide variations in both the heights and positions of peaks on the chromatogram and it was evident that the solution was extremely unstable. Because extensive degradation of the solution had occurred further attempts at its analysis were not undertaken. In experiment II an ethereal solution of products from this trap (excepting water) proved to be stable and was analysed.

E.II.3.a.iv: Gaseous products

Gaseous products from the -196°C trap were stored at -196°C. Samples were removed for a determination of their infra-red spectrum and for a determination of their mass spectrum. The remainder of the gaseous products was distilled into a small detachable trap containing methanol and cooled to liquid nitrogen temperature. The trap was detached, stoppered and

*Trade name

shaken while warming it to room temperature. The methanol solution was treated with 2,4-dinitrophenylhydrazine reagent. A copious orange precipitate was produced. The precipitate was filtered, well washed with dilute hydrochloric acid and water and finally dried. The 2,4-dinitrophenylhydrazone was reserved for its identification.

A discussion of the identification of individual components of the gaseous degradation products is given in section E.II.4.n.

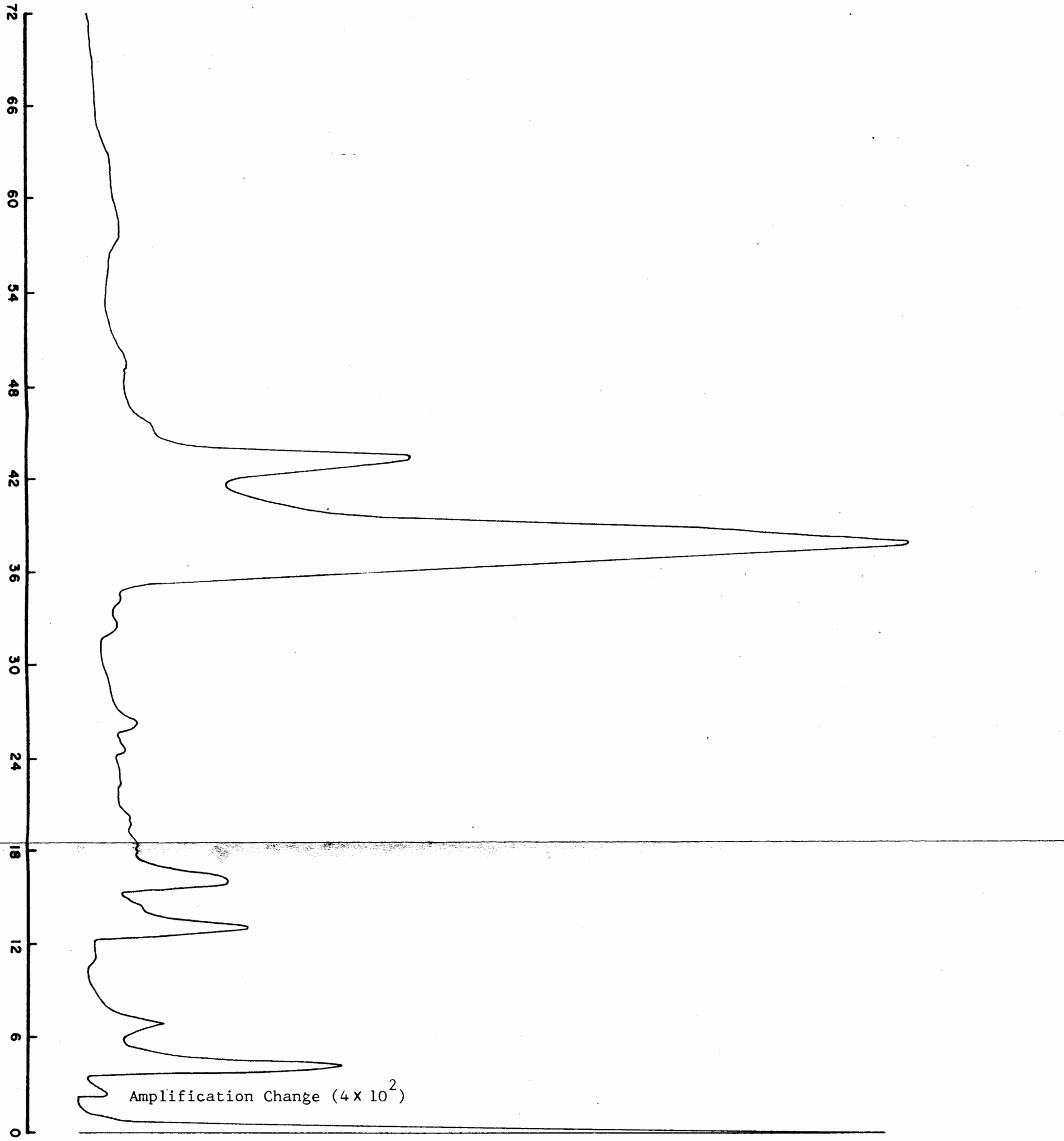
E.II.3.b: Experiment II

Experience gained in the previous experiment dictated the methods of analysis of the degradation products used successfully in Experiment II.

E.II.3.b.i: Reaction products from reaction vessel, fore-tube and -12.2°C trap

Experiment I showed that substantially the same products condense during degradation in the -12.2°C trap as in the fore-tube and reaction vessel except that higher molecular weight products predominate in the latter and more volatile products predominate in the former as would be expected. All the condensible products were, therefore, combined into one solution. Diethylether was used as solvent and proved to be better than either chloroform or methanol. No precipitation occurred in this solution which was, in addition, stable.

Preliminary work in Experiment I had shown the presence of acidic and basic reaction products. It appeared reasonable to attempt a conventional separation of the condensible products into acidic, basic and neutral components. This was all the more desirable as the chromatogram of the solution was



Sample: 0.5 mls. of products from -12.2°C trap, fore-tube and reaction vessel - Experiment II.

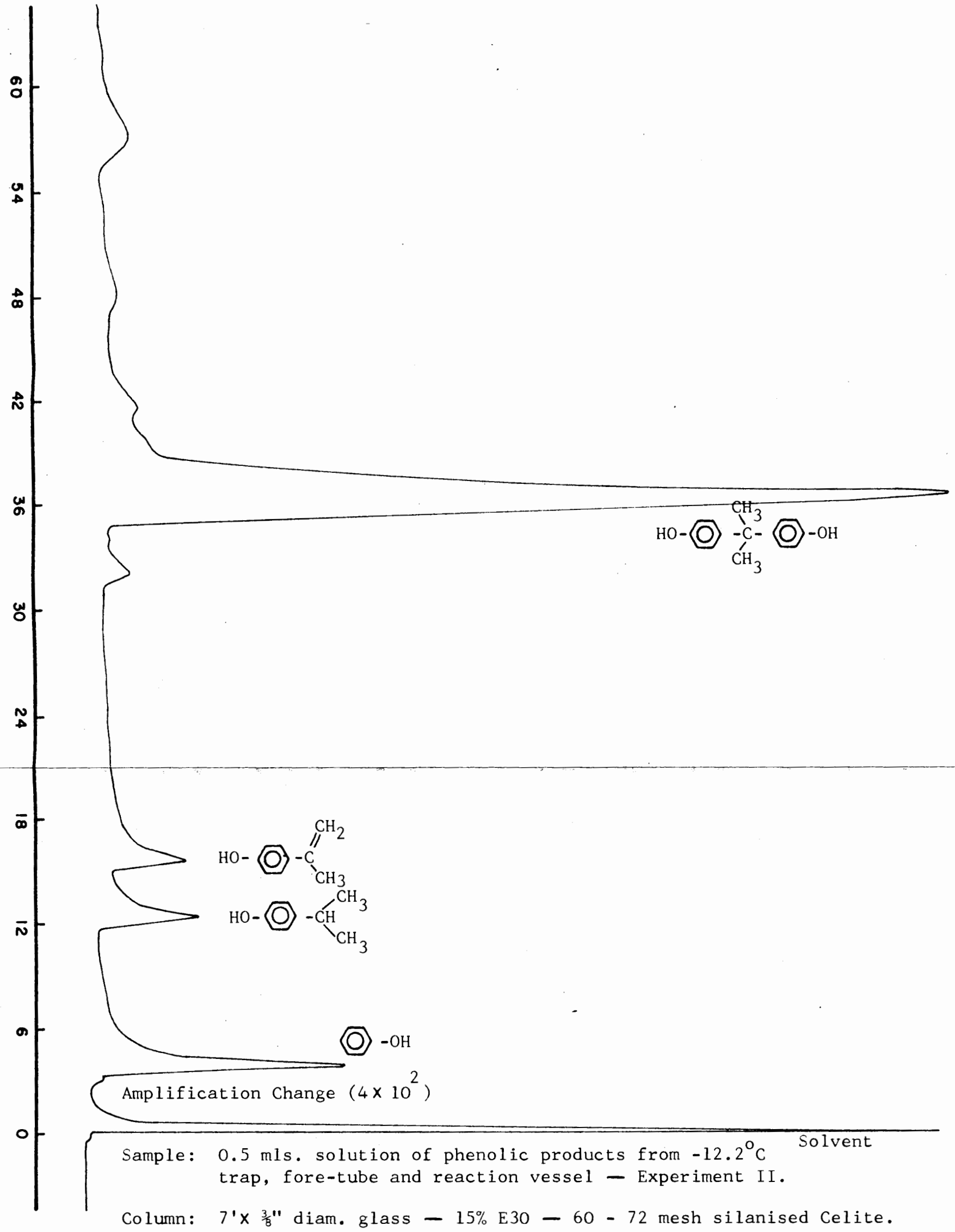
Column: 7'x ⅜" diam. glass — 15% E30 — 60 - 72 mesh silanised Celite.

Carrier: Nitrogen.

Flow Rate: 171 mls./min.

Temperature Programme: 105°C increased at 10 mins. at rate of 8°C/min. to 238°C.

Figure 22.



Sample: 0.5 mls. solution of phenolic products from -12.2°C trap, fore-tube and reaction vessel — Experiment II.

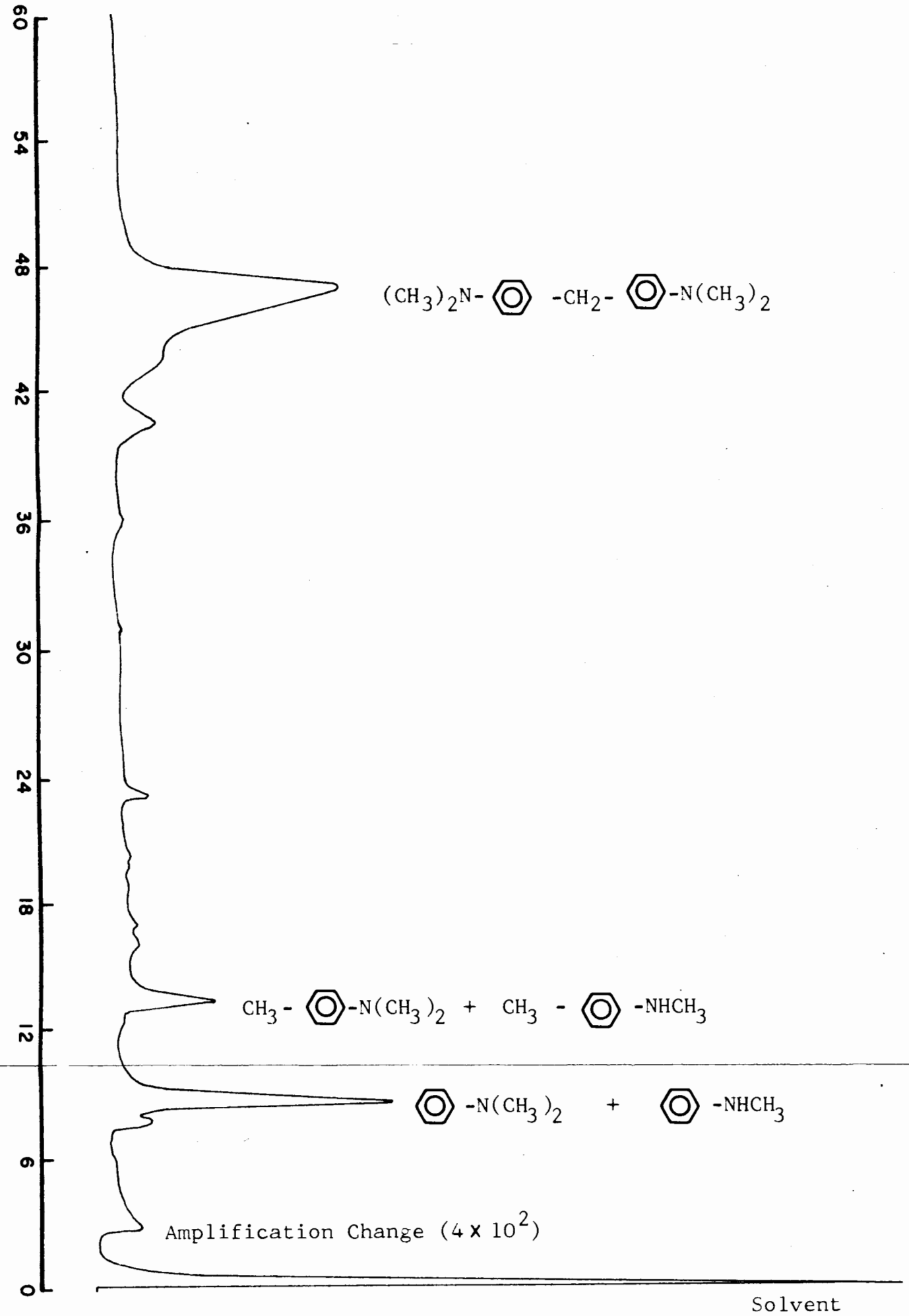
Column: 7' x ⅜" diam. glass — 15% E30 — 60 - 72 mesh silanised Celite.

Temperature Programme: 105°C increased at 10 mins. at rate of 8°C/min. to 238°C.

Carrier: Nitrogen.

Flow Rate: 171 mls./min.

Figure 23.



Sample: 0.5 mls. solution of basic products from -12.2°C trap, fore-tube and reaction vessel — Experiment II.

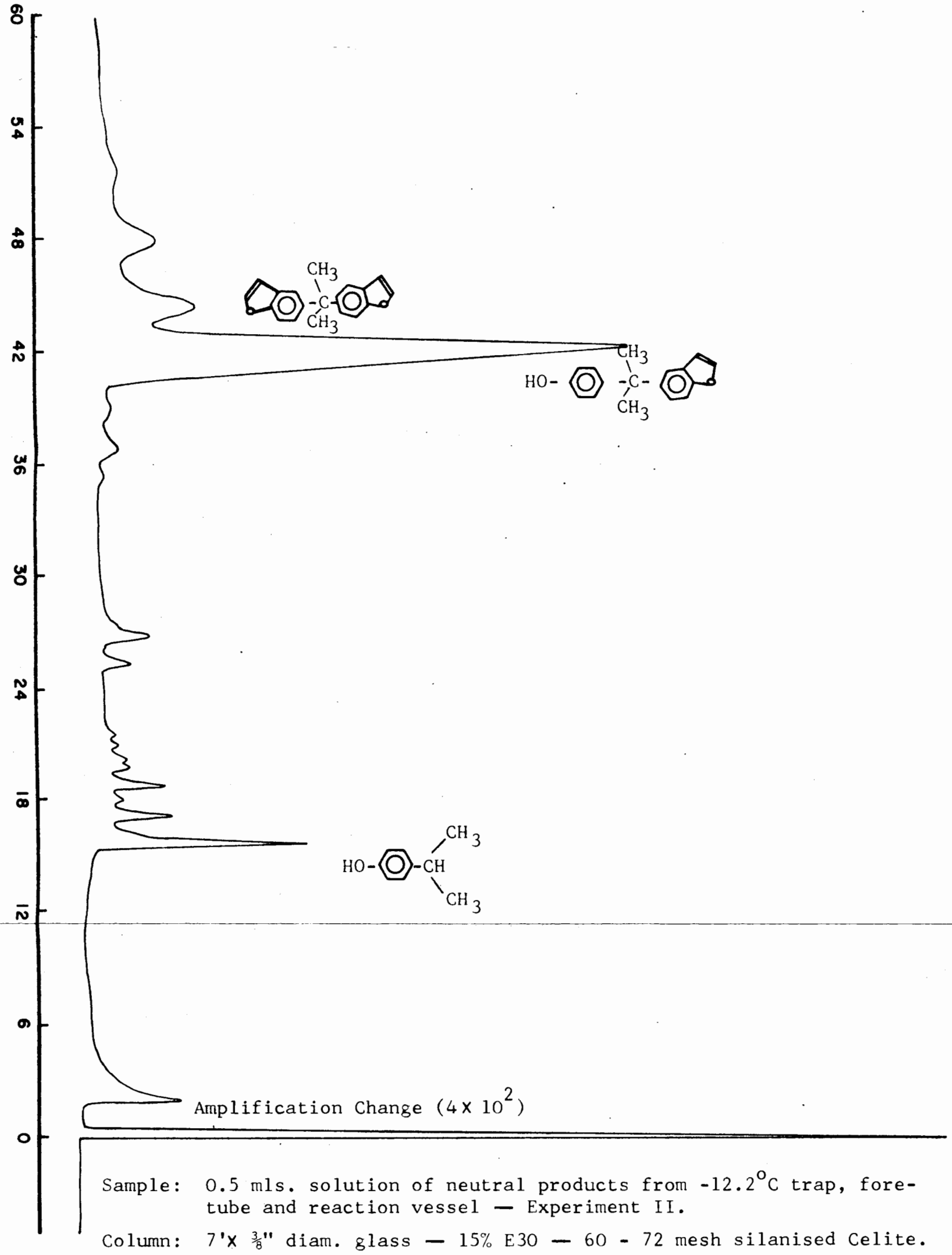
Column: 7' x ⅜" diam. glass — 15% E30 — 60 - 72 mesh silanised Celite.

Temperature Programme: 105°C increased at 10 mins. at rate of 8°C/min. to 238°C.

Carrier: Nitrogen.

Flow Rate: 171 mls./min.

Figure 24.



Sample: 0.5 mls. solution of neutral products from -12.2°C trap, fore-tube and reaction vessel — Experiment II.

Column: 7' x ⅜" diam. glass — 15% E30 — 60 - 72 mesh silanised Celite.

Temperature Programme: 105°C increased at 10 mins. at rate of 8°C/min. to 238°C.

Carrier: Nitrogen.

Flow Rate: 171 mls./min.

Figure 25.

crowded. (figure 22).

Before the separation of the condensible degradation products into acidic, basic and neutral components the original ethereal solution was chromatographed on a 7 feet long by ⅜" diameter glass column containing 15% E30* methyl silicone gum on 60 - 72 mesh silanised Celite*. The initial temperature of 105°C was increased 10 minutes after injection at a rate of 8°C/minute to 238°C. The chromatogram is shown in figure 22. After separation of the products into acidic, basic and neutral components the ethereal solutions which were all made up to 100 mls. volume were chromatographed under the same conditions. The chromatograms are shown in figures 23, 24 and 25. These chromatograms could then be correlated with that of the original solution.

The original ethereal solution of the condensible degradation products was shaken with 100 mls. of 10% sodium hydroxide solution. The aqueous layer was removed and titrated with dilute hydrochloric acid to a pH of exactly 7. (The pH was important since Experiment I had shown the presence of p-isopropenyl-phenol amongst the reaction products. This compound is susceptible to acid catalysed polymerisation. For the same reason the acidic components were removed from the original solution first i.e. before treatment of the solution with dilute hydrochloric acid to remove basic components). The neutral aqueous solution was extracted with ether and the aqueous layer discarded. After washing the ethereal solution of acidic components with 30 mls. of water, it was dried over anhydrous sodium sulphate, filtered and made up to a total volume

*Trade name

of 100 mls.

The ethereal solution remaining after removal of acidic components was shaken with 100 mls. of 7% hydrochloric acid. (More concentrated acid was not used since Experiment I had shown the presence of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane amongst the degradation products. The benzofuran structure is susceptible to polymerisation by strong mineral acids). The aqueous layer was basified and extracted with ether. The aqueous layer was discarded. The ethereal solution of basic components was washed with water, dried over anhydrous sodium sulphate, filtered and made up to 100 mls. total volume.

The ethereal solution remaining after removal of acidic and basic components was washed with four 50 mls. portions of water, dried over anhydrous sodium sulphate, filtered and made up to 100 mls. total volume.

A further reason for discarding chloroform as a solvent for these degradation products was the appreciable solubility of amine hydrochlorides in this solvent.

Each of the three solutions were chromatographed and fractions corresponding with individual peaks on the chromatograms were collected from repeated injections of the solutions.

Phenol, p-isopropylphenol, p-isopropenylphenol and Bisphenol A were identified as the major components of the solution of acidic condensible degradation products.

N-methylaniline, N,N-dimethylaniline, N-methyl-p-toluidine, N,N-dimethyl-p-toluidine and N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane were identified as the major components of the solution of basic

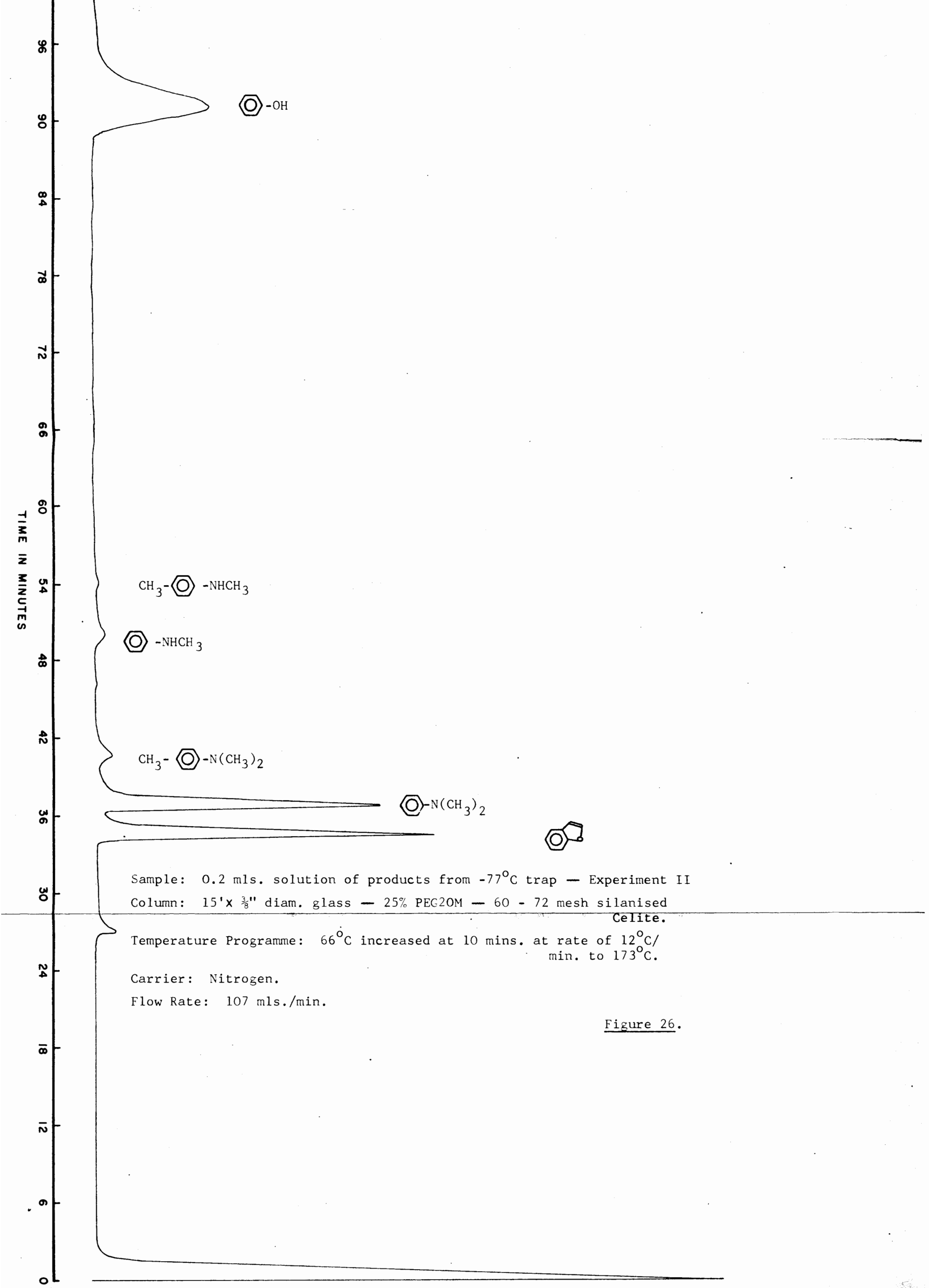
condensible degradation products.

p-Isopropylphenol, 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane and 2,2-bis-(benzofur-5-yl) propane were identified as the major components of the solution of neutral condensible degradation products. The appearance of p-isopropylphenol amongst the 'neutral' products showed that the separation of acidic and neutral components was not clear-cut. The appearance of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane (which contains an acidic hydroxyl group) amongst the neutral components may also appear strange. Subsequent work showed, however, that this compound is only slightly soluble in dilute sodium hydroxide solution. The separation of this compound and Bisphenol A by this means was fortunate since the two compounds are not separated on the chromatograph column (figure 22).

The chromatograms (figures 22,23,24 and 25) show that a large quantity of minor degradation products are present. A rough count of these put their number at approximately sixty-five. Their identification was not attempted. The experimental techniques used in this work were not suited to the analysis of very small quantities of substances. The possible analysis of the minor components of the degradation will be taken up in the Discussion (section F.7.i.). The comprehensive analysis of every degradation product would be a large undertaking. The identification of all the major degradation products was achieved.

E.II.3.b.ii: Reaction products from -77°C trap

Since a quantitative determination of the amount of water present amongst the reaction products had been



Sample: 0.2 mls. solution of products from -77°C trap — Experiment II

Column: 15'x ⅜" diam. glass — 25% PEG2OM — 60 - 72 mesh silanised Celite.

Temperature Programme: 66°C increased at 10 mins. at rate of 12°C/min. to 173°C.

Carrier: Nitrogen.

Flow Rate: 107 mls./min.

Figure 26.

made in Experiment I, attention was paid in Experiment II to the other products present in the -77°C trap. The ethereal solution of these products was chromatographed on the 15ft. long by ⅜" diameter glass column packed with 25% PEG 20M* polyethyleneglycol on 60 - 72 mesh silanised Celite*. The initial temperature of 66°C was increased 10 minutes after injection at a rate of 12°C/minute to 173°C. The chromatogram is shown in figure 26. Fractions corresponding with individual peaks on the chromatogram were collected from repeated injections of the solution. Repeated injections of the solution showed that the ethereal solution of the degradation products was stable.

Fairly large quantities of phenol, benzofuran and N,N-dimethylaniline were present. Smaller quantities of N-methylaniline and N,N-dimethyl-p-toluidine and a very small quantity of N-methyl-p-toluidine were also present.

E.II.3.b.iii: Gaseous degradation products

The gaseous products of the degradation were treated in the same way as those in Experiment I (section E.II.3.a.iv). The infra-red spectrum and the mass spectrum were identical with those of the gaseous products of Experiment I.

*Trade name

E.II.4: Identification of individual reaction products

E.II.4.a: Water

Water is the major degradation product. Lee's[35] work on the degradation of a low molecular weight commercial Bisphenol A type epoxy resin cured with p,p'-diaminodiphenylmethane also showed that water was the main product of this reaction. A quantitative determination of the percentages of water in the methanol solutions of the products collected in the -77°C and -12.2°C traps in Experiment I was made.

1 ml. aliquots of these solutions were titrated against standardised Karl Fischer reagent on an automatic Karl Fischer titrator. The Karl Fischer reagent was standardised against weighed portions of disodium tartrate dihydrate. Blank determinations of the water content of the methanol used for the solutions were made. The blank titres were subtracted from the titres of the solutions of reaction products.

The total water content of both solutions was 809.9 mg. (The solution of products from the -77°C trap contained the major portion of the water viz. 792 mg.). Assuming that the resin degraded was fully cured and assuming that water arises only from a dehydration reaction involving hydroxyl groups and, furthermore, that the only reaction of hydroxyl groups is to form water (section F.7.c.), the total possible quantity of water amongst the reaction products is 1241 mg.

Traces of water were also found in the -196°C trap in Experiments I and II (section E.II.4.a.vii).

E.II.4.b: Phenol

Phenol is produced in large quantities during the

degradation. Phenol was identified conclusively as a degradation product in preliminary work on the degradation of this resin/hardener system (Patterson-Jones and Smith).[50,51] Lee[35] also reported the presence of phenol as a product of the degradation of a commercial low molecular weight Bisphenol A type epoxy resin cured with p,p'-diaminodiphenylmethane. In Lee's work this product was not isolated.

Phenol was present in the fore-tube, in the -12.2°C trap and, in smaller quantities, in the -77°C trap. Phenol was identified by means of its infra-red spectrum. Confirmation of the identification was made in each case by comparisons of retention times of the degradation product and phenol when these were chromatographed under the same conditions (section D.II.5.a.).

E.II.4.c: p-Isopropylphenol

p-Isopropylphenol was reported by Lee[35] as a product of the degradation of a commercial Bisphenol A type epoxy resin cured with p,p'-diaminodiphenylmethane. Lee did not, however, isolate the product. This product was found in fairly large quantities in the fore-tube and the -12.2°C.trap.

p-Isopropylphenol was identified by means of its infra-red spectrum (Appendix B) and its NMR spectrum (Appendix C). Confirmation of the identification was made by thin-layer chromatography (section D.II.5.f.). The comparisons of the R_F values of the degradation product and p-isopropylphenol were made simultaneously on the same plate to avoid anomalies as was the case for all the products.

E.II.4.d: p-Isopropenylphenol

This compound was reported by Lee[35] to be a product of the degradation of a commercial low molecular weight Bisphenol A type resin cured with p,p'-diaminodiphenylmethane but was not isolated as a pure component in this work.

p-Isopropenylphenol occurs, in smaller quantities than those of p-isopropylphenol, in the fore-tube and in the -12.2°C trap.

The product was identified by means of its infra-red spectrum (Appendix D). Confirmation of the identification was provided by thin-layer chromatography of the degradation product and the synthetic product (section D.II.5.f.).

E.II.4.e: Bisphenol A

Bisphenol A (2,2-bis-(p-hydroxyphenyl)propane) has been reported as a degradation product by Lee[35] and as a possible degradation product by Stuart and Smith[58] who investigated the pyrolysis on a hot filament of a commercial Bisphenol A type resin cured with an aliphatic amine hardener. In neither case was the product isolated.

Bisphenol A is found in large quantities in the fore-tube and in smaller quantities in the -12.2°C trap. It is, after water, the second largest product of the degradation.

This product was identified by means of its infra-red spectrum (Appendix B) and its mass spectrum (Appendix D). Confirmation of the identification was provided by thin-layer chromatography (section D.II. 5.f).

E.II.4.f: N,N-Dimethylaniline

N,N-Dimethylaniline was identified in preliminary work on the degradation of this resin/hardener system (Patterson-Jones and Smith)[50,51]. This product had not been reported previously in any work on the degradation of aromatic amine cured epoxy resins.

N,N-dimethylaniline was found in the fore-tube, in the -12.2°C trap in fairly large quantities and was a major component of the products collected in the -77°C trap. The product was identified by means of its infra-red spectrum. Confirmation of the identification was provided by a comparison of retention times of the product and N,N-dimethylaniline when these were chromatographed under identifical conditions (section D.II.5.a.).

E.II.4.g: N-Methylaniline

N-methylaniline was found as a degradation product in preliminary work on this resin/hardener system (Patterson-Jones and Smith[50,51]). It had not been reported previously as a degradation product in any work on aromatic amine cured epoxy resins.

The mono-substituted aniline is found in smaller quantities than the disubstituted product. It appears in small quantities in the fore-tube, in larger quantities in the -12.2°C trap and in very small quantities in the -77°C trap. The product was identified by means of its infra-red spectrum. Confirmation was provided by a comparison of retention times of the degradation product and N-methylaniline when these were chromatographed under identical

conditions (section D.II.5.a.).

E.II.4.h: N,N-dimethyl-p-toluidine

This product has not been reported previously as a product of the degradation of aromatic amine cured epoxy resins.

N,N-dimethyl-p-toluidine appears in small quantities in the -12.2°C trap and in very small quantities in the -77°C trap. The substance was identified by means of its infra-red spectrum. A comparison of the retention times of the product and N,N-dimethyl-p-toluidine when these were chromatographed under identical conditions confirmed the identification (section D.II.5.a).

E.II.4.i: N-methyl-p-toluidine

N-methyl-p-toluidine has not been reported previously as a product of the degradation of aromatic amine cured epoxy resins.

N-methyl-p-toluidine was found in small quantities in the -12.2°C trap and in minute quantities in the -77°C trap. Its identification as a component of the products in the latter trap was made only by a comparison of retention times when the -77°C trap solution and a solution of N-methyl-p-toluidine were chromatographed under identical conditions, since the quantities of the product in this trap were too small for collection. The product collected in the -12.2°C trap was identified by means of its infra-red spectrum and by a comparison of the retention times of the product and N-methyl-p-toluidine when these were chromatographed under identical conditions (section D.II.5.a).

E.II.4.j: N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane

This product has not been previously reported in previous work on the degradation of aromatic amine cured epoxy resins.

N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane was found in large quantities in the fore-tube and in smaller quantities in the -12.2°C trap. It is, after water, Bisphenol A and 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane, the fourth largest degradation product.

This product was identified by means of its infra-red spectrum. Thin-layer chromatography provided confirmation of the identification (section D.II.5.f.).

E.II.4.k: Benzofuran

Benzofuran has not been reported previously as a product of the degradation of epoxy resins.

This product was not found in the fore-tube or the -12.2°C trap but was one of the major components of the products collected in the -77°C trap.

Benzofuran was identified primarily by means of its infra-red spectrum (Appendix B). Confirmation of the identification was provided by gas chromatography (section D.II.5.a) and thin-layer chromatography (section D.II.5.f).

E.II.4.l: 2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)propane

This compound has not been reported previously in the chemical literature.

After water and Bisphenol A, this product of the degradation is the third largest. Large quantities

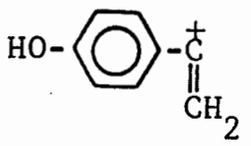
are found in the fore-tube and smaller quantities in the -12.2°C trap.

The elucidation of the structure followed a classical pattern. The use of instrumental techniques (infra-red spectrometry, mass spectrometry, nuclear magnetic resonance spectrometry and elemental analyses) led to the postulation of a structure. Synthesis of the compound having this structure was followed by a proof of the identity of the unknown and synthetic compounds.

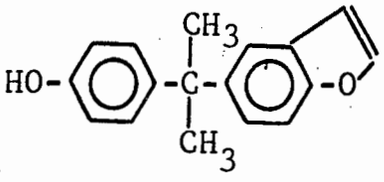
The infra-red spectrum of the crystalline product originally collected from the chromatograph column (Appendix B) showed the presence of an intra-molecularly hydrogen-bonded or, possibly, a single-bridge, inter-molecularly hydrogen-bonded hydroxyl group. This crystalline modification reverted on standing to the more stable crystalline form melting at 104°C whose infra-red spectrum is also shown in Appendix B. The synthetic product (section E.II.1.b) crystallised in this form.

The mass spectrum of the degradation product (section D.II.5.d, and Appendix D) fixed the molecular weight of the product at 252. The base peak (mass 237) suggested the loss of a methyl group from the structure. The NMR spectrum (Appendix C) showed the presence of two equivalent methyl groups, a hydroxyl group and a complicated aromatic system. The infra-red spectrum confirmed the presence of a hydroxyl group and indicated the presence of a hydrogen atoms adjacent to a double bond (C-H stretch region). The NMR spectrum suggested that the double bond formed part of an aromatic system. The presence of a phenolic hydroxyl group was suggested by the frequency of its absorption in the infra-red C-O stretch region. This was confirmed by the appearance

of a mass peak 119 in the mass spectrum which also appears in the mass spectrum of Bisphenol A and is due to the ion



The presence of the Bisphenol A nucleus was suggested on the basis of the above data. The evidence for the presence of the additional double bond led to the postulation of the structure



which had the required molecular weight.

This compound was synthesised (section E.II.1.b).

The structure of the degradation product was confirmed by proof of its identity with the synthetic compound. The identity of the degradation product with the synthetic product was proved by a comparison of their infra-red spectra (Appendix B), NMR spectra (Appendix C), mass spectra (Appendix D), melting points (section D.II.5.g) and by thin-layer chromatography (section D.II.5.f).

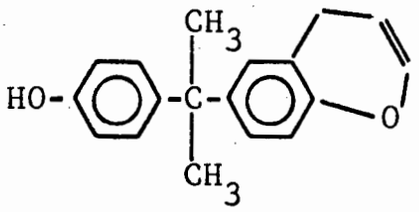
E.II.4.m: 2,2-Bis-(benzofur-5-yl)propane

This product has not been reported previously in the chemical literature. Small quantities are found in the fore-tube and very much smaller quantities in the -12.2°C trap.

The formation of this compound during degradation was expected since large quantities of 2-(benzofur-5-yl) -2-(p-hydroxyphenyl)propane were formed. The compound was not synthesised. Proof of its structure is provided by its mass spectrum (Appendix D and section D.II.5. d.ii) and infra-red spectrum (Appendix B). Since

confirmation of its structure was not provided by a comparison of the properties of the degradation product with those of a synthetic product, the presence of the product amongst the reaction products is described as 'suspected'. The quantities of the compound collected from the chromatograph column were too small for a determination of its nuclear magnetic resonance spectrum. The melting point of the compound was 80-81°C.

The mass spectrum showed that the substance collected from the chromatograph was not pure. Peaks of masses 252 and 237 indicate the presence of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane in the sample. The bis-benzofuryl compound peak on the chromatogram (figure 25) is not well separated from the peak for the mono-benzofuryl compound so that the contamination is not unexpected. The mass peaks 266 and 251 could indicate the presence as an impurity of 2-(1,4-benzopyran-6-yl)-2-(p-hydroxyphenyl)propane:



While peaks of these masses in no way constitute a proof of the presence of this substance amongst the reaction products, its possible formation may give a clue to the nature of some of the minor degradation products (section F.7.i). It is most likely that this impurity is present because it is not separated on the chromatograph from 2,2-bis-(benzofur-5-yl) propane. Since the quantity of product collected from the chromatograph was of the order of 6 mg. no attempt was made to purify it further.

E.II.4.n: Gaseous degradation products

The gaseous degradation products were collected in Experiments I and II in the -196°C trap. All these products were minor products of the degradation. The gaseous products in order of magnitude were acetaldehyde, chloromethane, carbon dioxide, ethene, carbon monoxide, ethane and methane together with traces of nitrogen and water. Lee[35] reported the presence of water, carbon monoxide, carbon dioxide, acetaldehyde, chloromethane and methane amongst the products of degradation at a temperature of 450°C of a commercial Bisphenol A type epoxy resin cured with p,p'-diaminodiphenylmethane.

E.II.n.i: Acetaldehyde

The 2,4-dinitrophenylhydrazone formed from a methanol solution of the gaseous degradation products (sections E.II.3.a.iv and E.II.3.b.iii) was that of acetaldehyde. This was proved by comparison of its infra-red spectrum with that of acetaldehyde 2,4-dinitrophenylhydrazone and by thin-layer chromatography (section D.II.5.f). The mass spectrum of the gases shows peaks at masses 44 (M^+), 43 (M^+-H) and 29 ($H\text{-}C{=}O^+$) characteristic of acetaldehyde. The infra-red spectrum of the gases (Appendix B) also shows the presence of large quantities of this product amongst the gases.

E.II.4.n.ii: Chloromethane

The presence of chloromethane was evident from the mass spectrum (Appendix D): mass peaks 50 and 52 (M^+), mass peaks 49 and 51 (M^+-H) and mass peak 15 (CH_3^+). The infra-red spectrum (Appendix B) confirmed the presence of chloromethane.

E.II.4.n.iii: Carbon dioxide

The mass spectrum (Appendix D) shows mass peaks 44 (M^{+}) and 22 (M^{++}) indicative of the presence of carbon dioxide. The infra-red spectrum (Appendix B) confirmed the presence of this product.

E.II.4.n.iv: Carbon monoxide, ethene and nitrogen

An accurate mass determination of the mass peak 28 in the mass spectrum of the gaseous degradation products (Appendix D) revealed the presence of carbon monoxide (mass 27.9949) ethene (mass 28.0313) and traces of nitrogen (mass 28.0061).

E.II.4.n.v: Ethane

An accurate mass determination of the mass peak 30 in the mass spectrum of the gaseous degradation products (Appendix D) revealed the presence of ethane and showed that formaldehyde was not present.

E.II.4.n.vi: Methane

The mass peak 16 in the mass spectrum of the gaseous degradation products (Appendix D) was due to the presence of small quantities of methane.

E.II.4.n.vii: Water

Traces of water were present amongst the gaseous degradation products. (mass peak 18 in the mass spectrum of the gaseous degradation products (Appendix D)).

E.II.5: Quantities of degradation products

Although water was the only product for which a quantitative analysis was made, a qualitative estimate of the quantities of other degradation products could be made from the size of peaks on the relevant chromatograms. Table 6 gives a summary of the products identified. The products are listed in order of magnitude.

Table 6

1.	Water	major product
2.	Bisphenol A	" "
3.	2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)propane	" "
4.	N,N,N',N'-Tetramethyl-p,p'-diaminodiphenylmethane	" "
5.	Phenol	" "
6.	p-Isopropylphenol	small quantities
7.	p-Isopropenylphenol	" "
8.	N,N-Diamethylaniline	" "
9.	2,2-Bis-(benzofur-5-yl)propane	" "
10.	N-Methylaniline	" "
11.	N,N-Dimethyl-p-toluidine	" "
12.	Benzofuran	" "
13.	N-Methyl-p-toluidine	" "
14.	Acetaldehyde	minor product
15.	Chloromethane	" "
16.	Carbon dioxide	" "
17.	Ethene	" "
18.	Carbon monoxide	" "
19.	Ethane	" "
20.	Methane	" "
21.	Nitrogen	traces

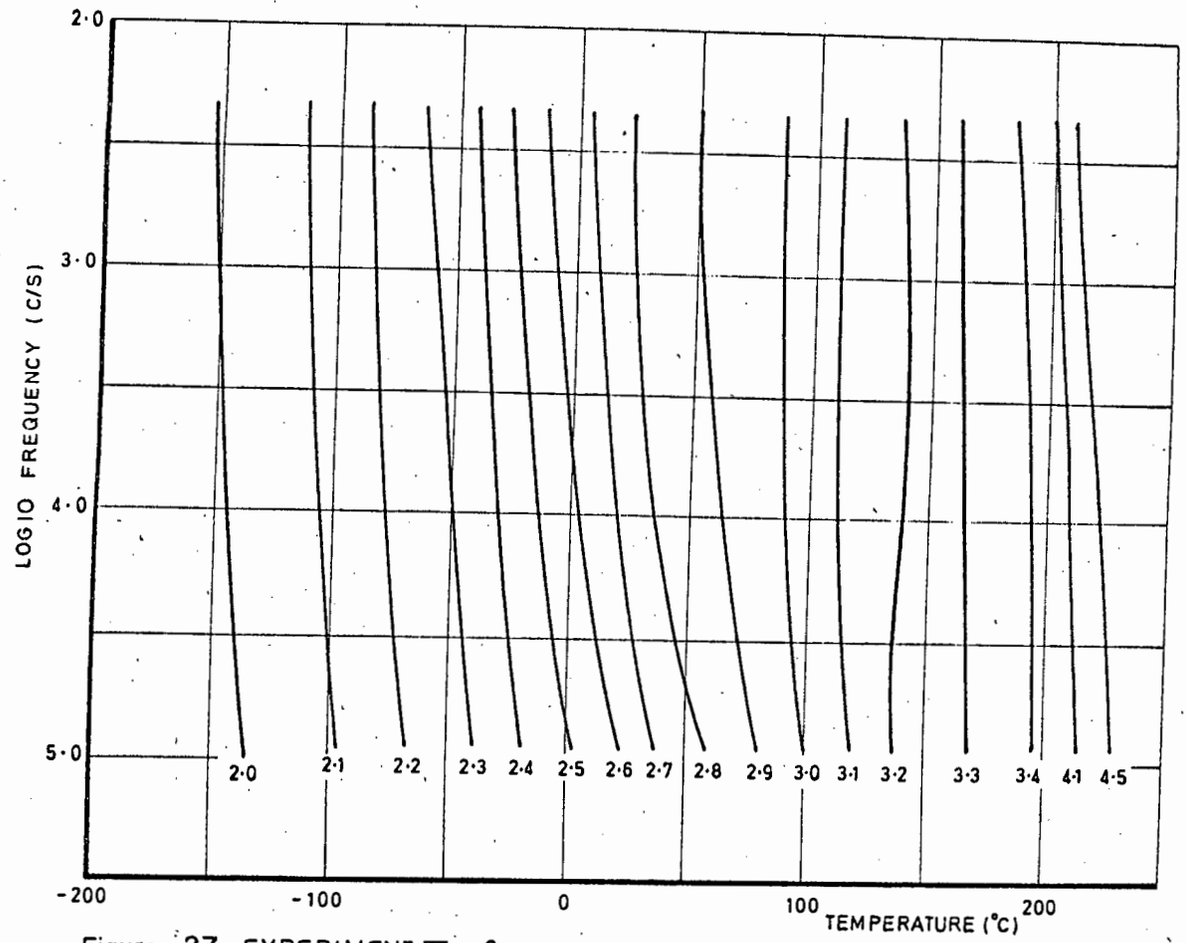


Figure 27 EXPERIMENT II ε

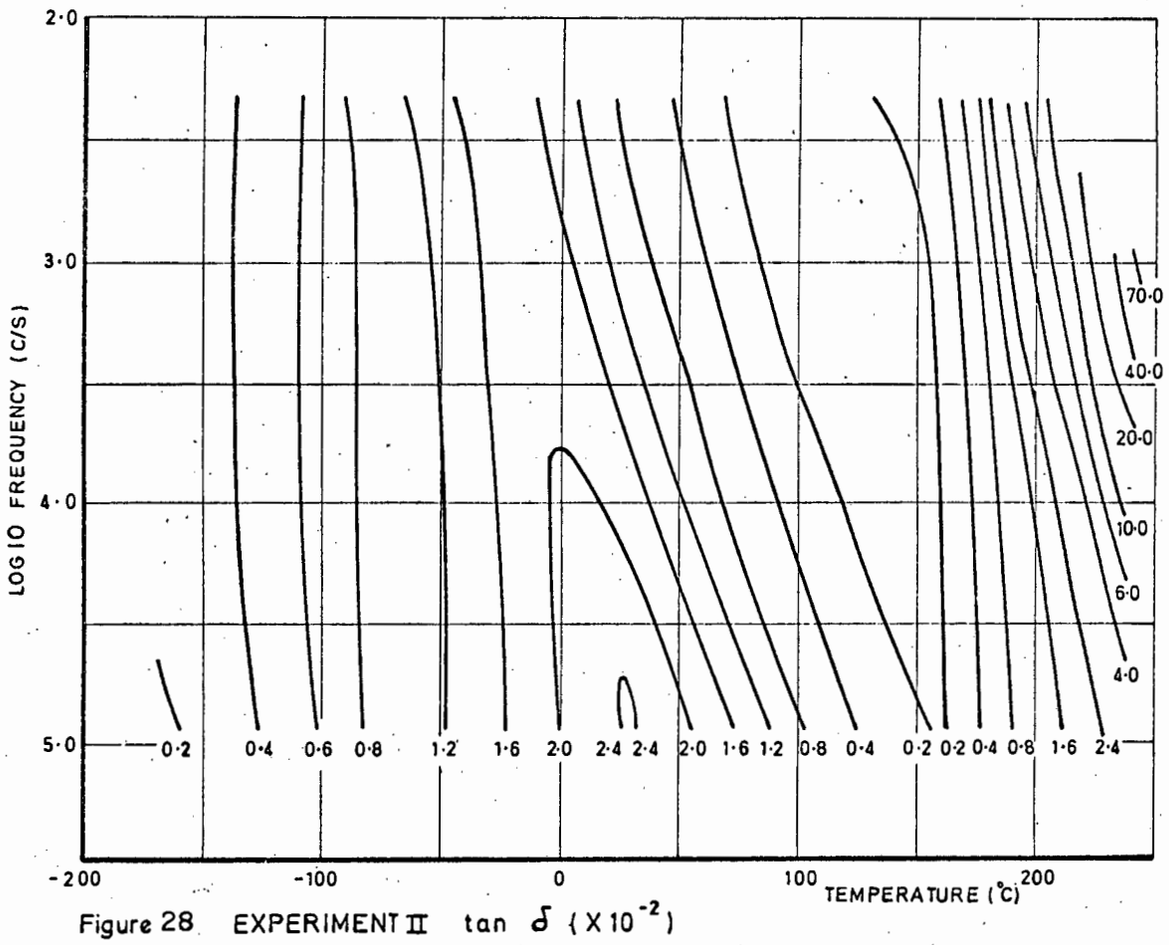


Figure 28 EXPERIMENT II tan δ ($\times 10^{-2}$)

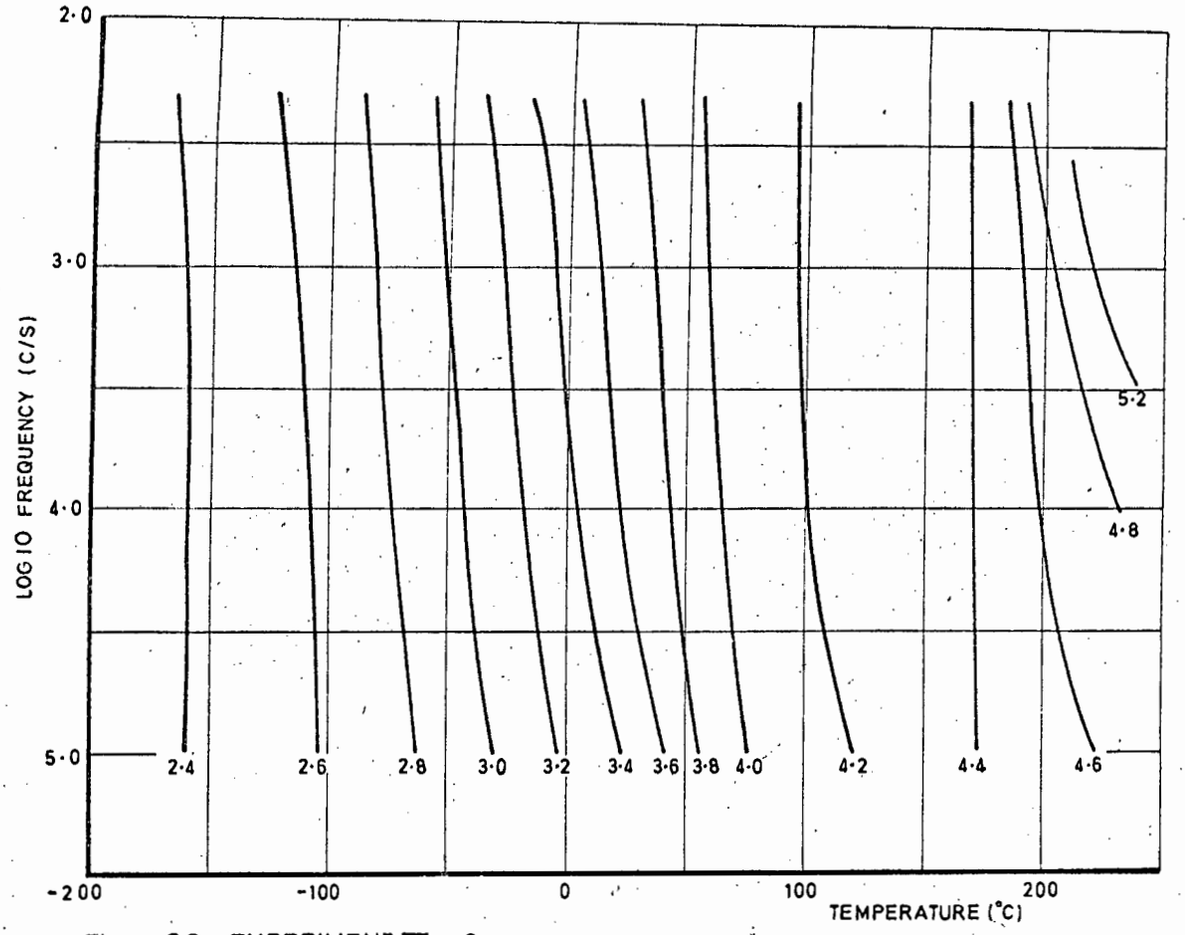


Figure 29 EXPERIMENT III ε

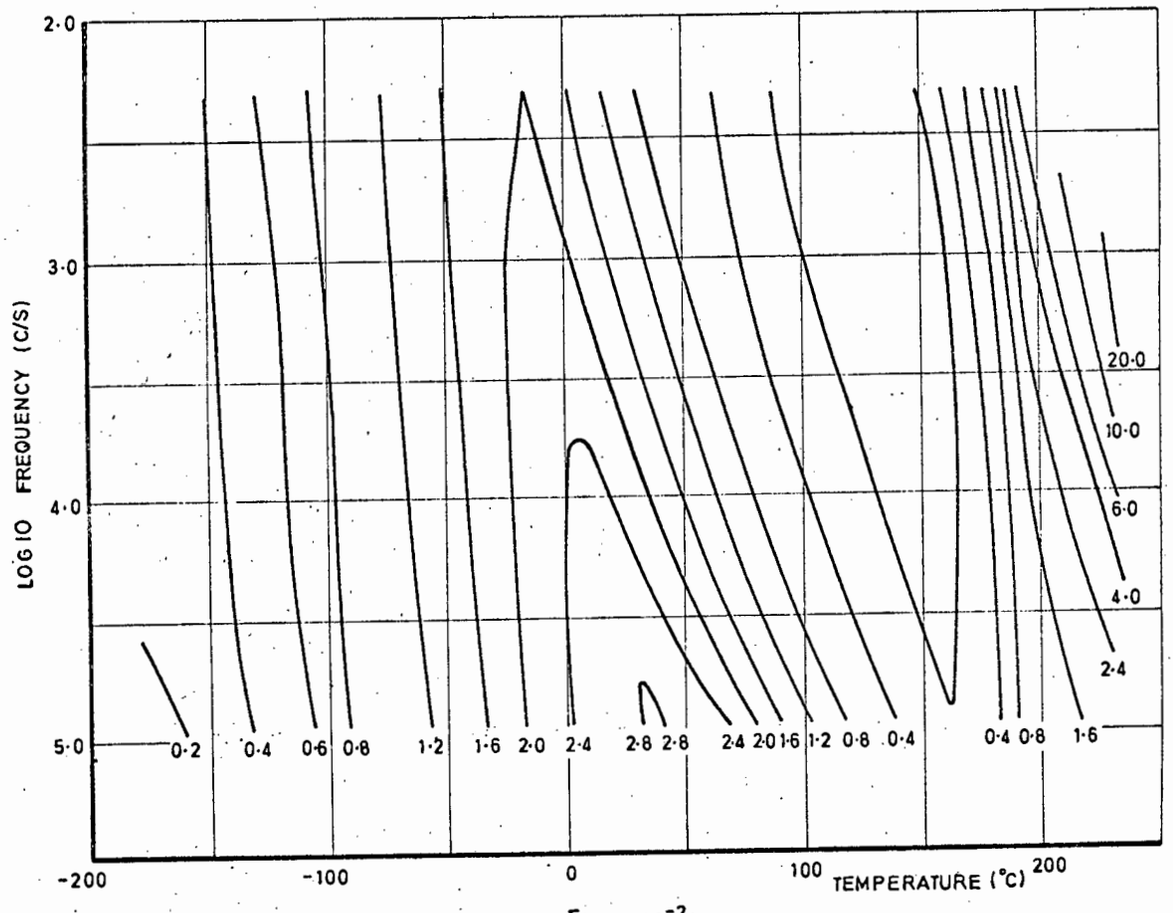


Figure 30 EXPERIMENT III tan δ ($\times 10^{-2}$)

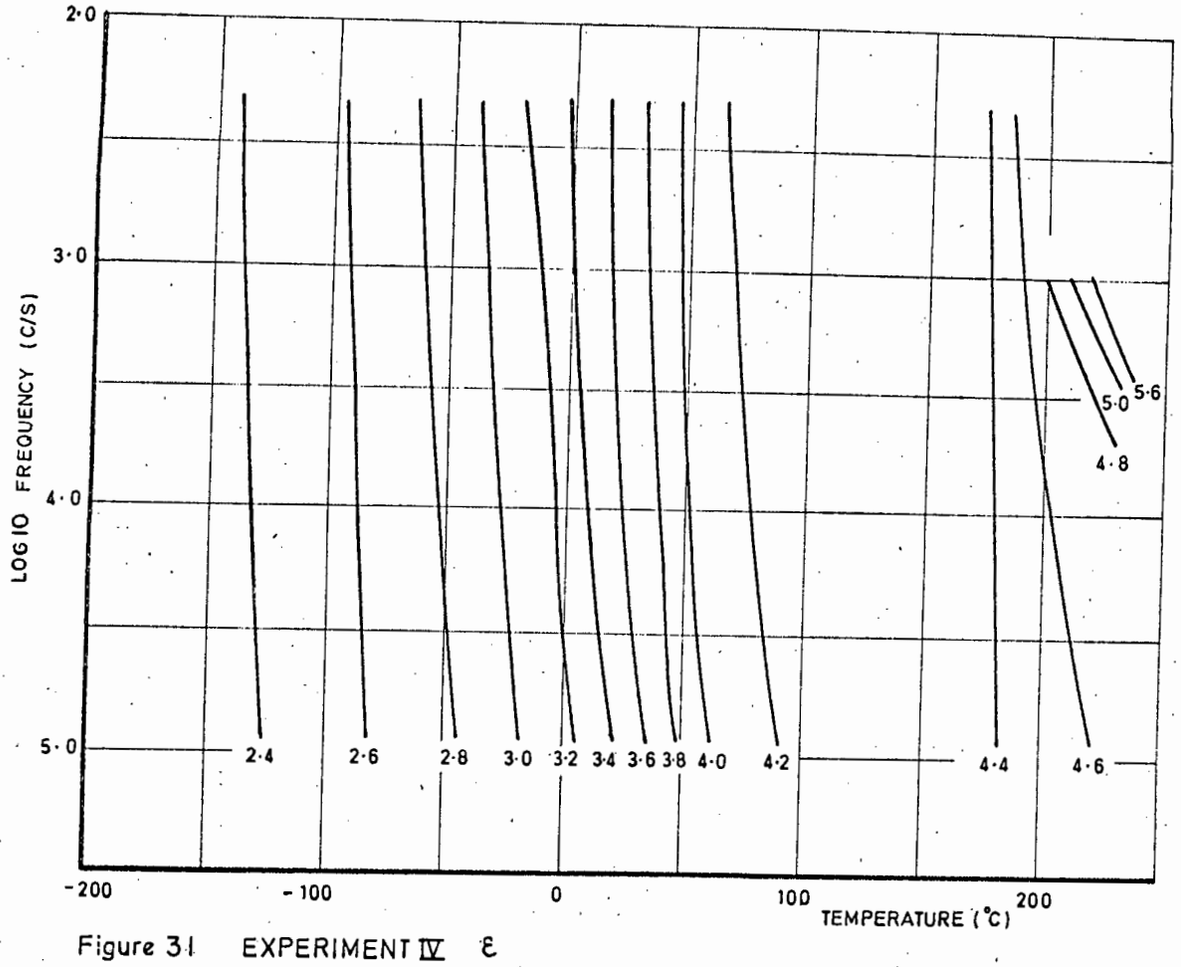


Figure 31 EXPERIMENT Ⅳ ε

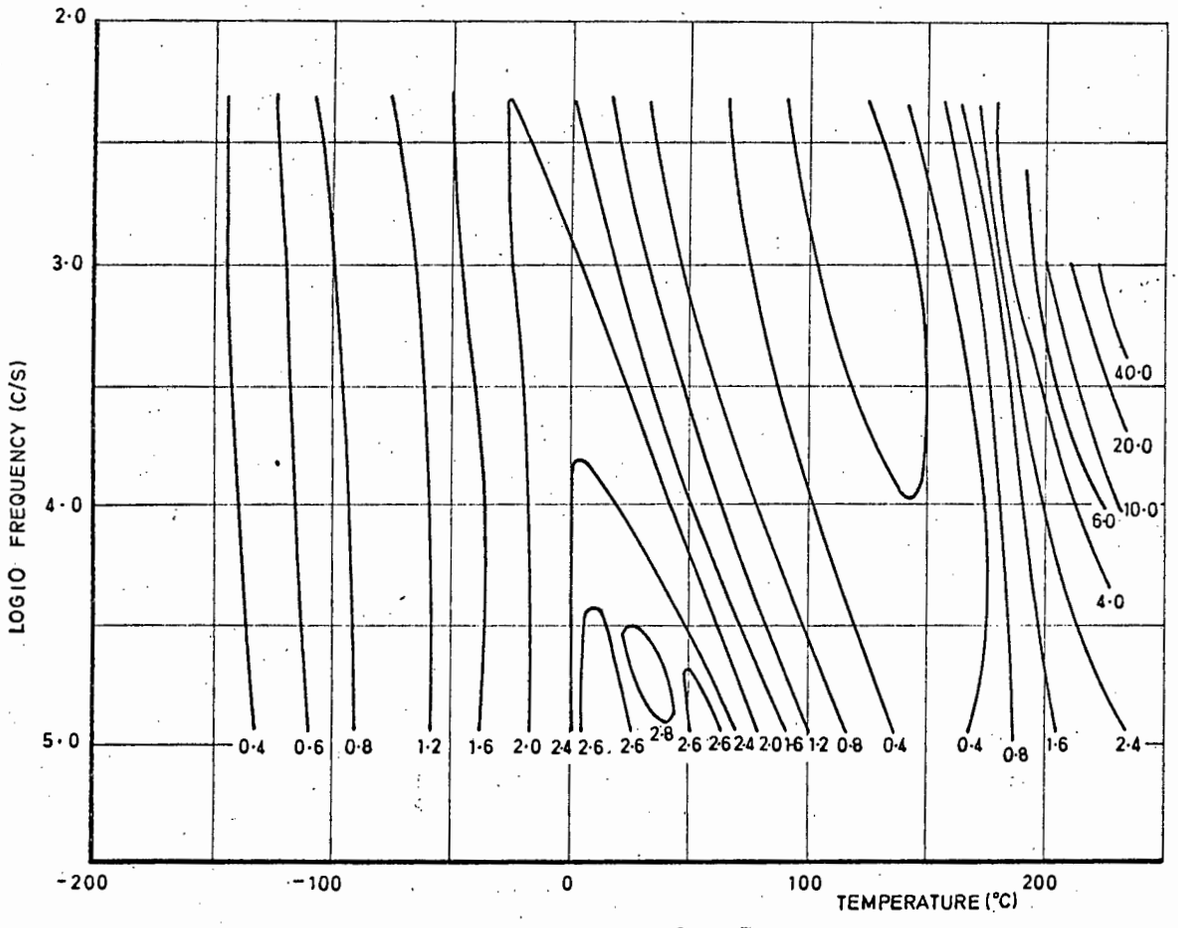


Figure 32. EXPERIMENT Ⅳ tan δ ($\times 10^{-2}$)

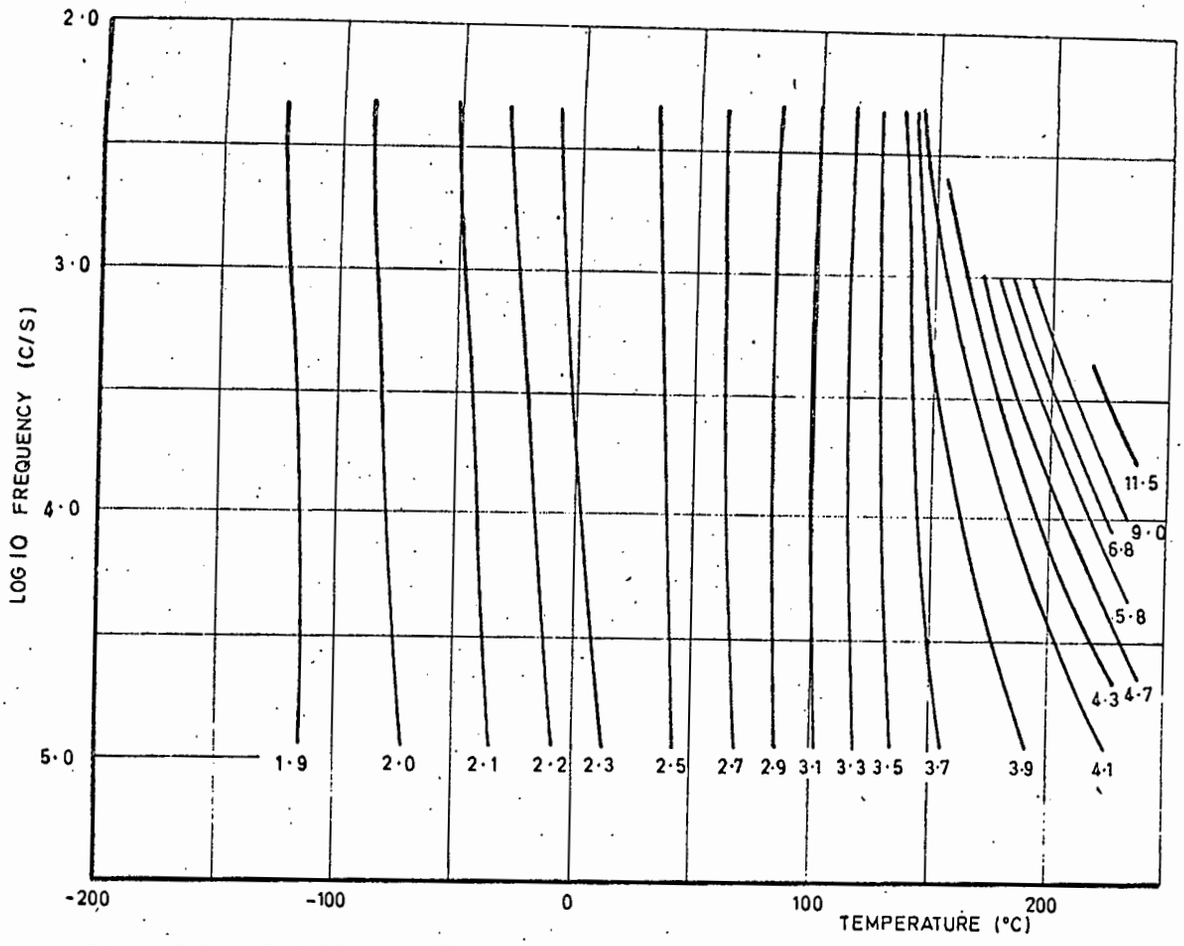


Figure.33 EXPERIMENT Ⅴ ε.

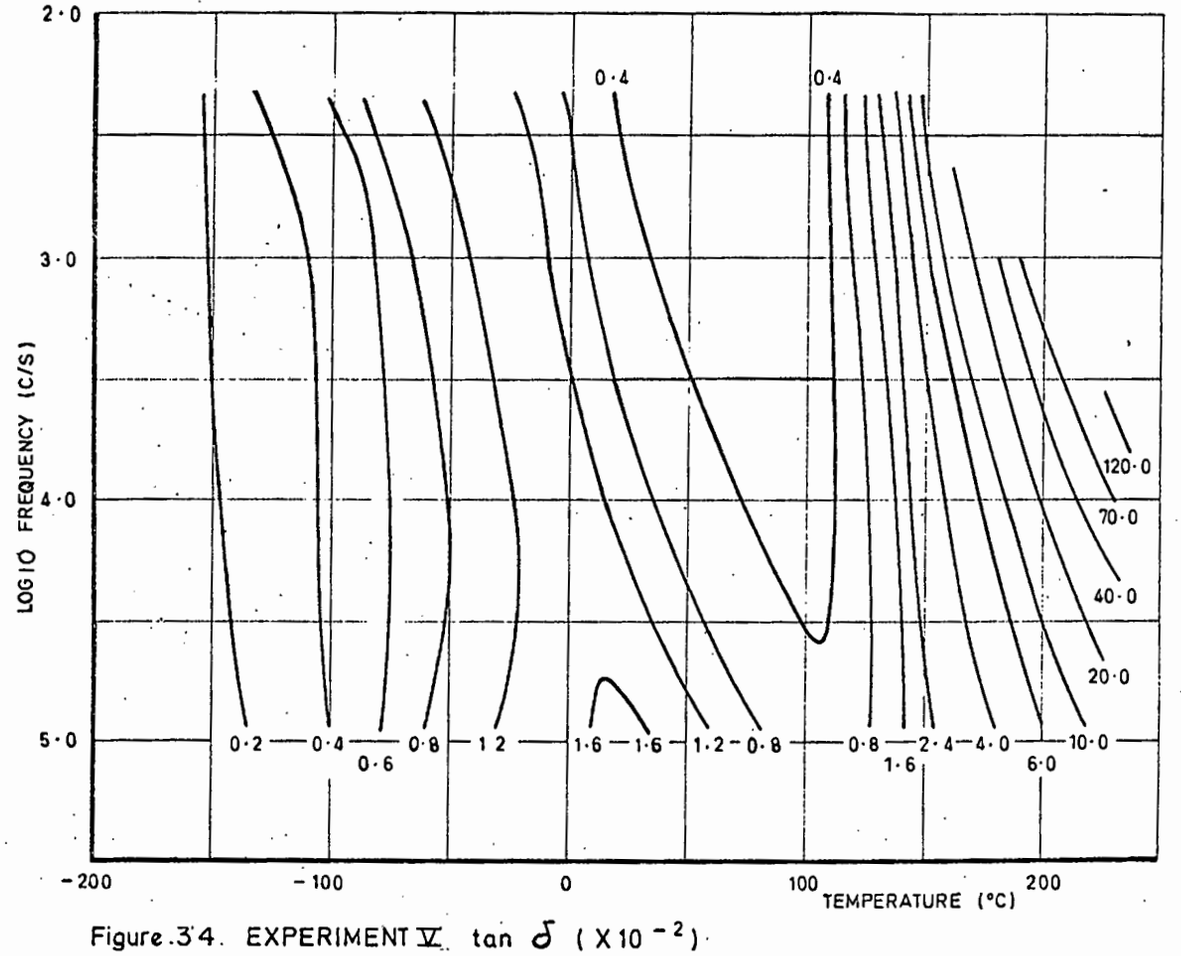


Figure.34. EXPERIMENT Ⅴ. $\tan\delta$ ($\times 10^{-2}$)

F: Discussion and Analysis of Results

F.1: Dielectric results

The dielectric results of Experiments II, III, IV and V are presented as contour plots of the real part, ϵ', of the complex dielectric constant and the loss tangent, tan δ, as functions of frequency and temperature, in figures 27-34. The results for Experiment II are for a fully cured resin which has not been degraded. The term 'fully cured' will be considered in detail in section F.2. The results for Experiments III, IV and V are for increasingly degraded specimens.

The results for all four experiments show that in the frequency/temperature range considered the samples are characterised by two distinct dispersion regions;

(i) a low temperature region, and

(ii) a high temperature region.

The low temperature region, or β-region as it will be termed in this discussion, is broad and is characterised by relatively low values of tan δ. A plot of log f_{max} versus $\frac{1}{T}$ (where f_{max} is the frequency of maximum absorption and T is the absolute temperature) for the results of the undegraded sample is roughly a straight line and gives an apparent activation energy of some 16½ k cals/mole. In Mikhailov's[42] terminology this value characterises the β-region as due to a dipole-radical type of loss as opposed to a dipole-elastic type of loss. On this basis the loss is therefore probably due to the movement of a dipole essentially independently of the main chain and this is consistent with the temperature/frequency range in which the loss occurs.

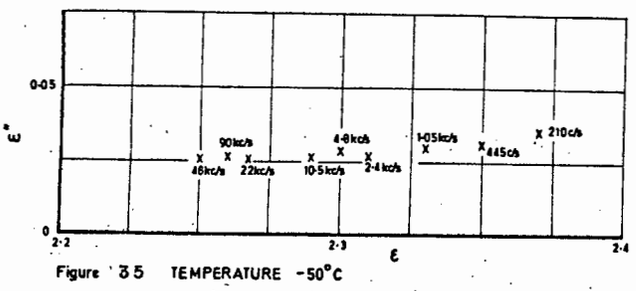


Figure 35 TEMPERATURE −50°C

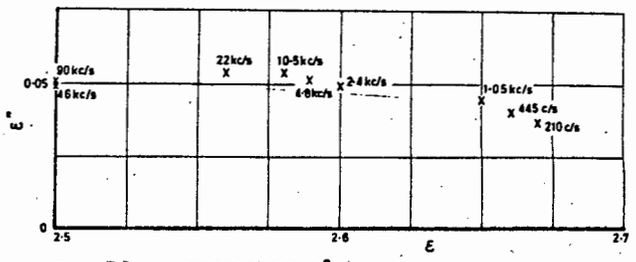


Figure 36 TEMPERATURE 0°C

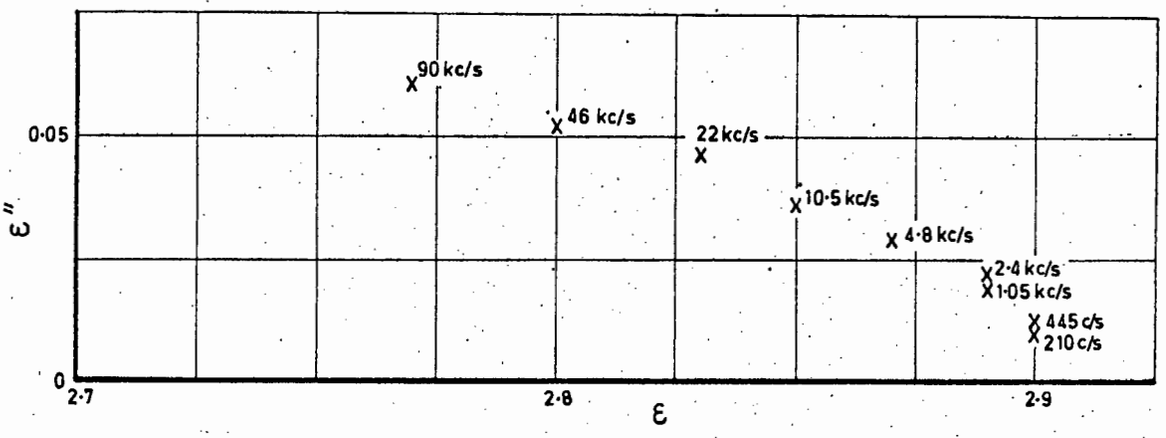


Figure 37 TEMPERATURE 50°C

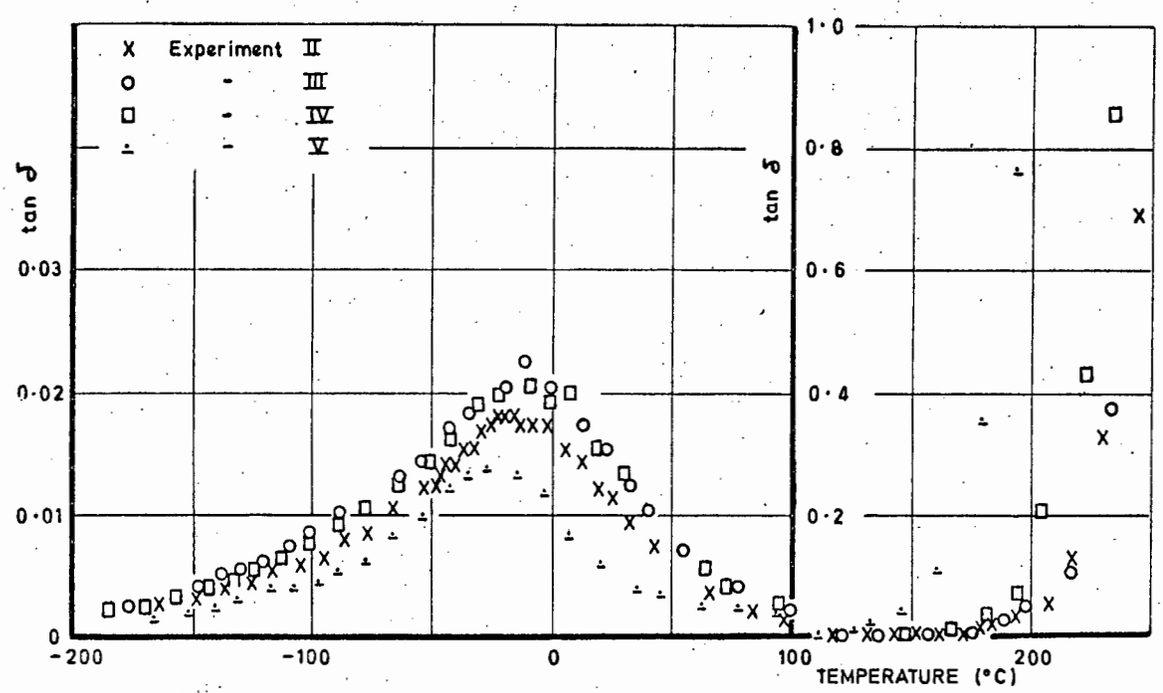


Figure 38 EXPERIMENT II, III, IV and V

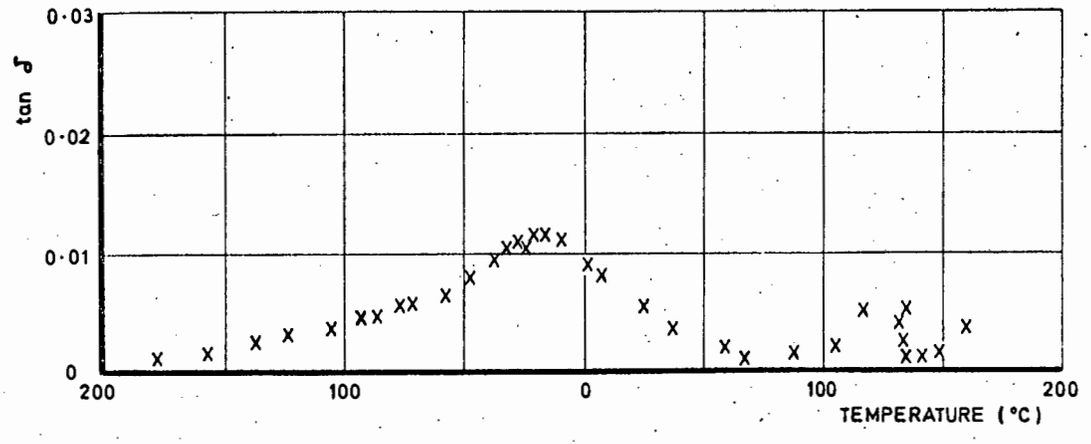


Figure 39. EXPERIMENT 1.

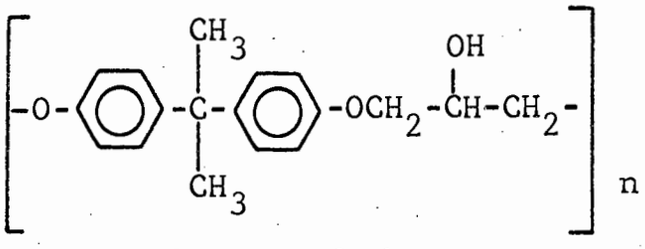
Cole-Cole plots of the locus of the complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ in the complex plane for the sample of Experiment II at temperatures of $-50^{\circ}C$, $0^{\circ}C$, and $50^{\circ}C$ are shown in figures 35, 36, and 37 respectively. It is at once clear that the absorption is not an ideal Debye-type absorption. While the locus of the complex dielectric constant at temperatures of $0^{\circ}C$ and $50^{\circ}C$ might conceivably be a circular arc in the experimental range covered, that at $-50^{\circ}C$ is very clearly not since it appears to be concave upwards. It is therefore likely that, if the full frequency range were available, the locus of the complex dielectric constant would not be a circular arc, or even a skewed arc. Since the theories so far developed have only been for these cases, further theoretical analysis is impossible. It is likely, however, that the process giving rise to this dispersion region is a complicated one. In view of this, the apparent activation energy for the process quoted earlier is of dubious significance.

There is a hint in the results that the loss peak is a result of two overlapping loss peaks. This is clear in figure 38 which shows tan δ as a function of temperature at a frequency of 1.05 kc/s for Experiments II, III, IV and V. This is most obvious in Experiment IV which concerned a degraded sample, but is also discernible in the result of Experiment II. This may imply that at least two processes are operative in giving rise to the loss.

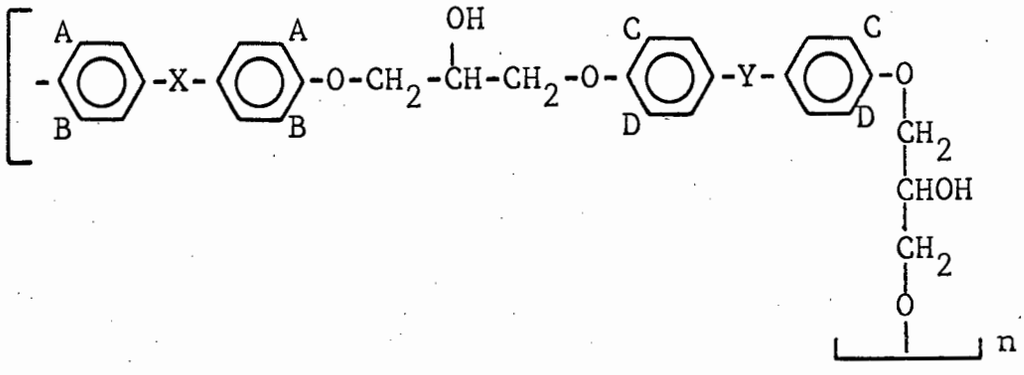
From a consideration of the chemical structure of the cured resin (section F.2) it is clear that the only dipolar group which could be responsible for the β-loss region is the hydroxyl group. As far as the resin

network is concerned, these groups are the only pendant dipolar groups which could be responsible for a dipole-radical type of loss; the movement of any other dipole in the network structure would necessarily involve a change in the configuration of the network involving a dipole-elastic type of loss.

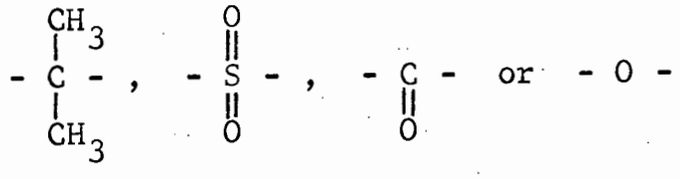
Reinking et al.[55] and Hoorn[30] studied the loss regions associated with linear polymers of structure related to that of the resin in this investigation. Reinking et al. studied polymers of the structure



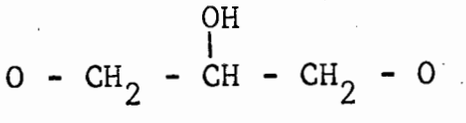
and Hoorn polymers of the structure



where A, B, C and D were hydrogen, methyl or chlorine and X and Y were

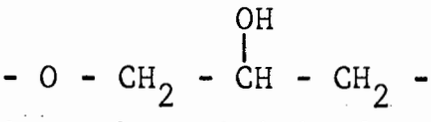


The common structural feature is the



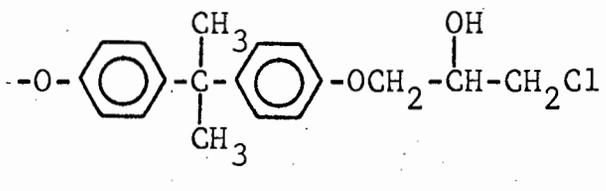
portion of the molecule joined by inflexible groups. Because of the structural similarity of these polymers,

which were amorphous, with the resin used in this investigation, they would be expected to show similar loss regions. This was the case. Both Reinking et al's polymers and Hoorn's polymer without ring substituents showed two loss regions, a low temperature and a high temperature region. Both authors, however, attributed the low temperature loss region to movement of the 'glyceryl portion of the chain'. If this is taken to mean segmental motion of the



portion of the chain, this is to be criticised. Such a motion would give rise to a dipole-elastic type of loss and would necessarily, therefore, characterise the main glass transition temperature of the polymers since the groups joining this portion of the chain are inflexible. This is not consistent with the type of loss shown in the low temperature region nor with the frequency - temperature ranges in which it occurs. It appears, therefore, more reasonable to attribute the low temperature region loss to rotation of the hydroxyl group independently of the main chain. Confirmation of this is to be found in Reinking et al's paper.[55] Esterification of the hydroxyl group removed the loss completely. Evidently the bulkier ester groups cannot move when the polymers are in the glassy state.

There are other dipolar groups present in the fully cured system which could give rise to dipole-radical type losses. These include residual epoxide and amine groups and impurities such as

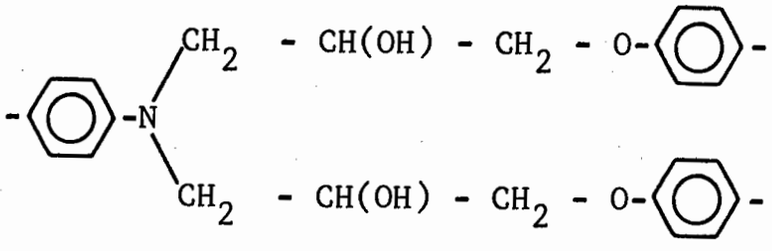


The concentration of any of these groups is, however, so small that their contribution to the dielectric properties is not likely to be measurable.

Figure 39 shows the results of measurements of tan δ as a function of temperature at a frequency of 1.05 kc/s for the resin disc of Experiment I. For reasons given in section F.2., it was clear that the disc was by no means fully cured. In figures 39 and 40 it is clear that as the discs were more fully cured so the maximum value of tan δ in the β-loss region increased, the greatest value being recorded for the disc of Experiment III which had in fact been cured up to a temperature such that some slight degradation had occurred. For increasingly degraded specimens in Experiments IV and V the maximum value of tan δ in the β-loss region decreased. The analytical results showed that water is the main degradation product. As will be discussed later (section F.7.c.), water is formed in dehydration reactions involving the hydroxyl group. Although it would be unreasonable to postulate that the concentration of hydroxyl groups in the resin is the only factor controlling the extent of the absorption, the results of this investigation showed clearly a direct relation between the concentration of hydroxyl groups, which increases with increasing cure and decreases with increasing degradation, and the maximum value of tan δ in the β-loss region. This was taken as further evidence that the hydroxyl groups were responsible for the loss.

Work by Dannenburg[18] on the spectra in the near infra-red of epoxide resins during cure with an amine hardener showed that the hydroxyl groups in the cured

resin can be hydrogen bonded. A consideration of the possible configurations of the unit



showed that mutual hydrogen bonding between the two hydroxyl groups is possible; hydrogen bonding of the hydrogen of one hydroxyl group with both the ether oxygen and the nitrogen are also possible. In addition to these possibilities, hydrogen bonding between the hydroxyl hydrogen and oxygen and even nitrogen atoms of neighbouring chains is possible. The characteristics of orientation of the hydroxyl group in an electric field are governed by the change in energy accompanying the orientation which in turn depends upon the forces involved. The many different possibilities for hydrogen bonding of the hydroxyl group are probably responsible for the broadness and the non-ideality of the β-loss region. The underlying property is the random nature of the resin structure which is one of its chief characteristics.

The high temperature region or α-loss region has two main characteristics. The first is that in the temperature range covered no local maximum or peak in values of tan δ was found. It was shown that degradation, as measured by weight loss, occurred at temperatures above 240°C approximately so measurements were not continued much above this temperature. The second was that very high values of tan δ, approaching 1, were recorded in this temperature range. It should be noted that the assumptions implicit in the

reduction of the dielectric properties to a statement of ϵ' and tan δ as functions of frequency and temperature (in particular that of linear behaviour) are unlikely to be valid when such values of tan δ are found and, for this reason, the values of tan δ recorded are of qualitative significance only.

The α-dispersion region was associated with the resin network. Since no peaks in the values of tan δ were found it was not possible to characterise the region as due to dipole-elastic losses on an apparent activation energy approach. The reasons for characterising the α-loss region as being a property of the network are reserved for section F.3.

Kobale and Löbl[34] gave the dielectric properties of a commercial epoxide resin cured with an anhydride hardener, tetrahydrophthallic anhydride. As in this investigation two distinct loss regions were found. The low temperature region was a broad region characterised by low maximum values of tan δ. An apparent activation enthalpy for the process was quoted as 11 k cals/mole, activation entropies being too small to measure. From a consideration of the chemical structure of the cured resin network Kobale and Löbl concluded that movement of the OH group was responsible for this loss region. In support of this they quote activation enthalpys for the movement of the OH dipole in Terylene and ice. This is to be criticised. The forces involved in the highly cross linked random structure of the cured epoxide resin with all the attendant different possibilities of hydrogen bonding and differing steric barriers are likely to be very different from the forces involved in the linear partially crystalline Terylene and the

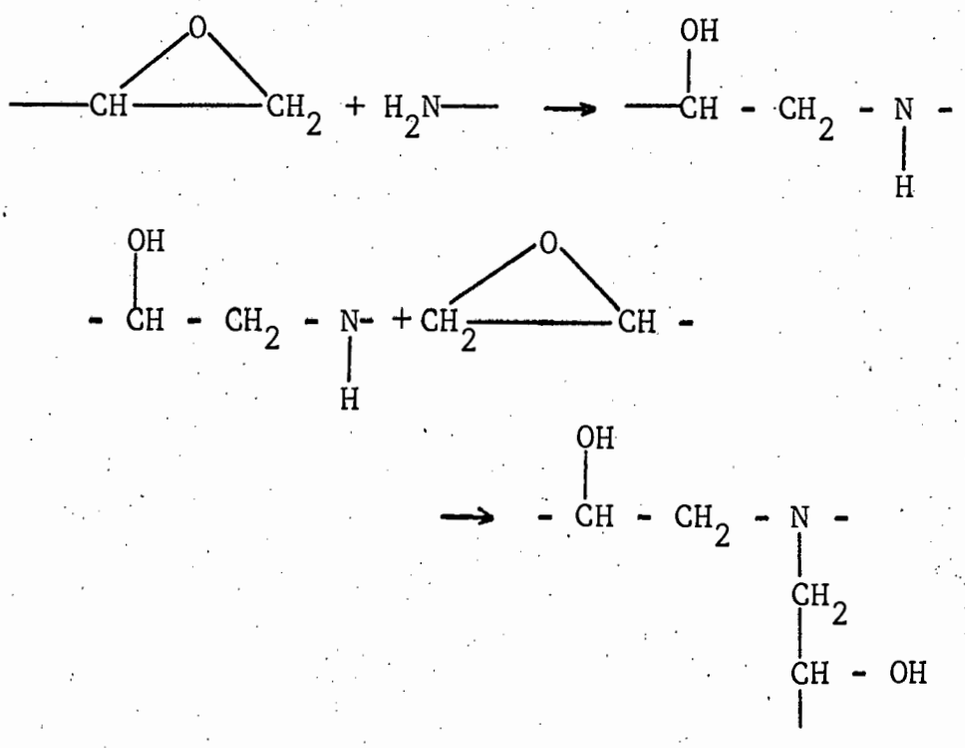
perfectly ordered molecular crystal, ice. The rough agreement of the values for the activation enthalpy for the movement of the OH dipole in these three solids is probably fortuitous and, in any event, is not sufficient evidence to identify the process.

In contradistinction to the results of this investigation, Kobale and Löbl found well defined peaks in the values of tan δ for the high temperature loss region, the maximum values of tan δ being in the region of 0.1. They showed clearly the relation of this region with the properties of the network and characterised the losses as dipole-elastic losses.

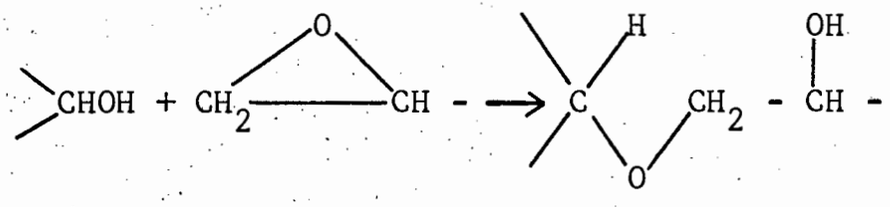
Kobale and Löbl also gave some results for an epoxide resin cured with p,p'-diaminodiphenylmethane. Two dispersion regions were found corresponding with the results of this investigation. It is significant that for this system no maxima in the tan δ curves were shown for the α-loss region. The authors make no mention of this fact and the system is not discussed in detail.

F.2: Cure

The overall chemical reactions involved in the curing of dge-BPA with DDM are fairly simple and involve the reaction of epoxide groups with both the primary and secondary amine groups:

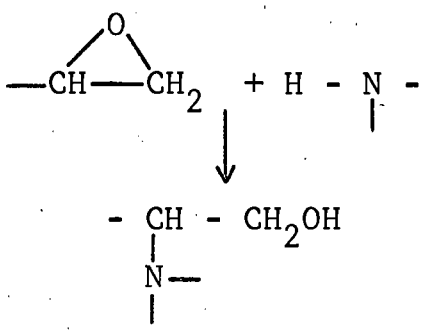


Work on model compounds by Schechter, Wynstra and Kurkjy[36] showed that etherification of the aliphatic hydroxyl by epoxide groups



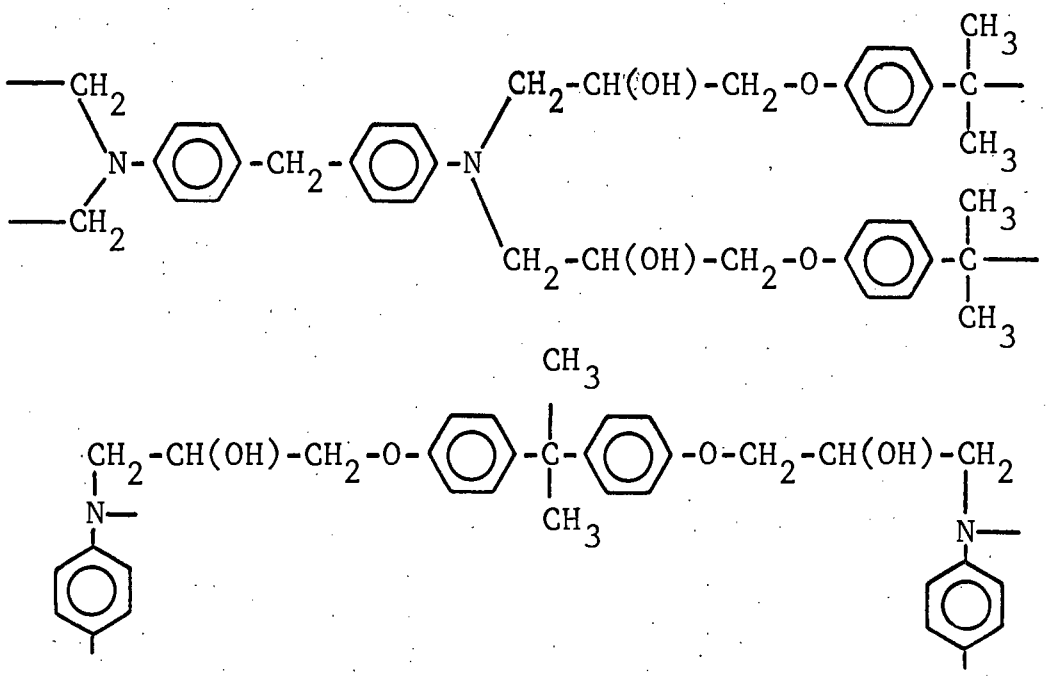
does not occur to any appreciable extent. This is supported by the fact that optimum properties are obtained for this resin/hardener system when equi-equivalent amounts of hardener and epoxide resin, calculated on the basis of one epoxide group for every basic hydrogen present, are used.

Smith's[58] results showed that the abnormal ring-opening reaction

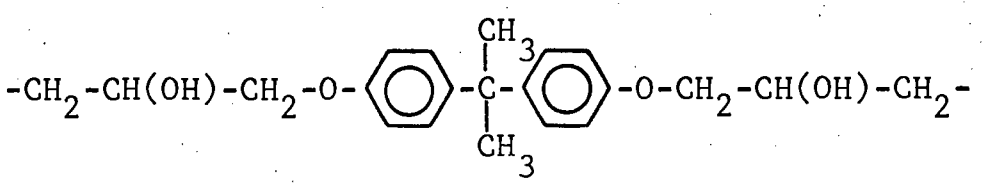


did not occur to any appreciable extent.

As cure proceeds molecules with the structure



are built up. Consideration of the possible conformations of the unit



show that the number of pairs of these units joined by the same two nitrogen atoms is small and that a truly random structure is found.

At a certain stage, the gel point, a sharp increase in viscosity of the system marks the appearance of a large three-dimensional network molecule which forms a phase which is essentially distinct from the liquid phase which existed before, which now co-exists and which consists of small molecules and small fragments of addition products. Molecular motion and hence chemical reaction are by no means halted; the cure process continues by reaction in the remaining liquid phase, by an increase in the size of the network and by an increase in the degree of cross-linking of the network. Reaction is accompanied by a decrease in the amount of liquid phase present and an increase in the rigidity of the network.

The network may be characterised by its glass transition temperature which, for the purposes of this discussion, may be defined as the temperature below which segmental motion of the network is not possible. The word 'motion' implies the specification of frequency if an attempt is made to measure this property. It is clear that as cure proceeds the role of the cure reaction shifts from that of building onto the network to increasing the cross-linking of the molecule. If cure is carried out isothermally there may come a time when the degree of cross-linking and the amount of liquid phase present are such that the glass transition temperature of the network corresponds to the cure temperature.

At this stage cross-linking must practically cease, for this implies molecular motion and this is frozen in all but any remaining liquid phase. The results of Experiment I (figure 39) exemplify these predictions.

The disc used in these measurements was cured finally at 130°C. The graph of tan δ /temperature shows a rise in values of tan δ as 130°C is approached but the expected peak at 130°C is not realised. The value of tan δ at 135°C is lower than would be expected and successive measurements at this temperature show a progressive decrease in tan δ . The temperature of measurement was raised to 160°C and then lowered. The results appear to indicate a peak in the region above 160°C.

These results are simply explained on the basis of the above predictions. The disc originally cured at 130°C cured up until the glass-transition temperature corresponded to the cure temperature. As the temperature of measurement approached 130°C a rise in tan δ was noted which signified the approach of a peak in tan δ characterising the glass transition. As the temperature was raised further, however, molecular motion became possible and the sample became unstable as further cure reactions occurred until the glass-transition temperature corresponded to the new cure temperature i.e. the temperature of measurement. Raising the temperature to 160°C provided the opportunity for further cure until the glass-transition temperature corresponded to this temperature. Subsequent measurements at temperatures below 160°C confirmed the apparent appearance of a peak characterising the glass transition temperature somewhere above 160°C.

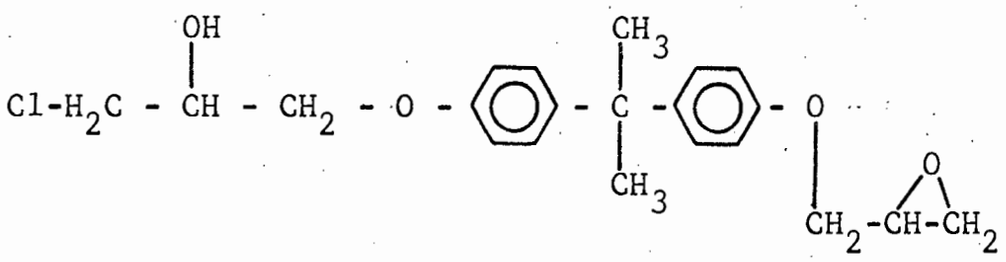
Information in a technical bulletin by CIBA(ARL) Ltd.[11] on the properties of a low molecular weight epoxy resin cured with DDM confirms the correspondence of the deflection temperature (which is related to the glass-transition temperature) and the cure temperature.

Recent papers by Fava[22] and Fisch et al.[25] have confirmed the correspondence of isothermal cure temperature of epoxide resins with the glass transition temperature of the cured sample. Both papers confirm that when a sample of resin is cured isothermally, the cure reactions can proceed only so long as the mobility of the network allows reaction. As the glass transition temperature approaches the isothermal cure temperature reaction is inhibited and finally completely halted. Despite the presence of unreacted epoxide groups in the partially cured sample no further reaction takes place in the glassy state.

Information gained in Experiment I dictated the heat treatment of discs used in further experiments. The discs were given an initial cure at 95°C. Since the discs were to be post-cured/degraded at temperatures above 240°C there appeared no point in post-curing for any length of time at temperatures below these. A feature of the apparatus was that in the degradation vessel the final post-cure/degradation temperature was reached relatively slowly, allowing ample time for cure as the temperature increased. Increased cure implied an increase in the glass-transition temperature by increased cross-linking, and hence increased cure temperatures were necessary to provide for molecular movement and hence reaction. All this was achieved progressively in the degradation vessel. Oxidation, which becomes appreciable in air at 180°C, was precluded.

The sample which exists after cure at an elevated temperature consists mainly of a random three-dimensional network molecule. Ideally the sample would consist of nothing else. In fact it is obvious that when cure has reached a certain stage it may be

impossible for two pendant unreacted groups (one epoxide, the other amine) to meet and react. To put it more succinctly, the probability of co-ordinated segmental motions of the network which would allow previously separated pendant groups to approach closely and react is prohibitively small. In the 'fully-cured' resin, therefore, there must exist unreacted epoxide, primary and secondary amine groups and possibly very small numbers of unreacted dge-BPA and DDM molecules. The concentration of all these is very low. In addition to these impurities, molecules originally of the structure



which were present in the dge-BPA will form pendant groups through reaction of the one epoxide group. Other trace impurities may be present.

Recent work by Cuthrell[16,17] has thrown considerable doubt on the conception of cured epoxide resins as macroscopically homogeneous materials as the previous comments would suggest. Studying principally an anhydride cured polyol-modified Bisphenol A type resin, Cuthrell showed that the partially cured resin consists of roughly spherical floccules of highly cross-linked material packed in a regular array in an interstitial matrix of material of low conversion. The formation of the floccule was thought to be colloidal in origin. The size of the floccules varied with the curing conditions from 20 to 90 μ and over. While it would be unwise on the basis of this work to assume that all cured epoxide

resin systems and, in particular, that studied in this investigation are similar in nature to those studied by Cuthrell, the idea that the cured resin consists of a network extending throughout the sample may not be correct. This raises doubts about the degree of cure in "fully cured" resins. There is much evidence e.g. Fisch et al.[23] that in properly cured resins the degree of conversion of epoxide groups approaches 100%. That complete conversion can never be realised has been discussed. Questions that now arise assuming that Cuthrell's findings are general for epoxide resins concern the chemical nature of the interstitial fluid and whether in the final stages of cure the interstitial fluid largely disappears with a corresponding coalescence of the floccules. At present in the absence of further data these questions remain unanswered and there is some uncertainty regarding the macroscopic structure and chemical structure (which is necessarily connected) of the resins.

F.3: Discussion of the α-loss region

The α-loss regions recorded for the samples of Experiments II, III, IV and V were regions in which sharp rises in both tan δ and ε were noted for rises in temperature. The maximum in the values of tan δ which is usually associated with a dispersion region was not noted. Measurements could not be extended to higher temperatures in an attempt to locate a peak since the temperatures were such that degradation occurred.

The temperature/frequency range of the α-loss region is such that it would be unlikely to be due to dipole-radical type losses even if there were a dipole available other than the hydroxyl group to provide for such a loss. It appears reasonable, therefore, that the loss is associated with movement of the network i.e., that it is due to relaxation of the network. This cannot provide the whole explanation of the results however, since a simple relaxation of the network should provide definite peaks in tan δ / temperature curves.

Weight loss measurements showed that degradation is appreciable at temperatures around 240°C. The identity of the main degradation products found in this investigation excepting water which all contain phenyl groups, is such that degradation must involve the resin network; further, it must involve a break down of the network by the scission of chemical bonds to produce these chemical species. Their production from unreacted amine or epoxide groups is not reasonable firstly, because of the extremely low concentration of these in a fully cured resin and, secondly, because their chemical nature is not compatible with this origin. The production of separate small molecules

from the network presupposes at least two scissions of chemical bonds in the network. These are unlikely to be simultaneous and so it is evident that appreciable scission of chemical bonds in the network occurs in the 240°C temperature range, some of which leads by further scission to the appearance of small molecules.

The possible fates of two free radical ends produced by the homolytic scission of a chemical bond in the network are many. The most obvious and most likely is recombination to form the same chemical bond. For this reason, it seems likely that appreciable scission occurs, only a small fraction of which leads to the production of small molecular weight products.

The 'free ends' produced by scission which exist in the resin at elevated temperatures must contribute to the dielectric properties if they are free to oscillate in the field. Providing the network is above its glass transition temperature such motion is possible. The abnormality of the α-loss region is attributed to the existence of these free ends at the temperatures involved. That the superposition of dielectric loss due to the motion of the free ends on top of the dielectric loss due to relaxation of the network provides for the measured very high values of tan is clear since, as the temperature of measurement is raised, so scission is a more likely event and the rate of production of free ends is increased. The instability of the samples at elevated temperatures is almost certainly due to the same effect.

At any particular temperature the rate of production of free ends by scission of network bonds is roughly constant. If their only fate was to recombine then eventually an equilibrium would be set up such that the concentration of free ends is constant.

This may be the case at the lower end of this temperature region (210°C - 220°C). Any irreversible process such as stabilisation of the free radical by isomerisation, by splitting off a smaller molecule, or by disproportionation, which follows scission means that the concentration of free ends may not be constant. This implies that the dielectric properties in this temperature region are a function of time. This is a further reason why the data on tan δ and ϵ for this temperature range are of qualitative significance only.

The results for the α-loss region recorded in this investigation for an amine cured epoxide resin appear to contrast strongly with those recorded by Kobale and Löbl[34] for an anhydride cured epoxide resin. The α-loss region in the latter investigation was shown clearly to be a relaxation phenomenon. The extra chemical stability of anhydride cured epoxide resins compared with amine cured resins is well known. In the case of an anhydride cured resin it appears that at the glass transition temperature no significant scission occurs. Alternatively, it is possible that a full α peak in the tan δ /temperature curve was not found due to the fact that correct temperature and frequency conditions were not attained. In view of the wide range of temperatures and frequencies used this explanation of the observed phenomena seems less probable than that based on degradation of the network, which is further described below.

Just as an increase in the cross-linking of the network causes a shift of the glass transition to higher temperatures so it would be expected that any breakdown of the network which involves the scission of chemical bonds would cause a corresponding lowering

of the glass transition temperature. The results of Experiments II,III, IV and V confirm this. (figure 38). The results for Experiments II and III show tan δ vs. temperature curves which are practically colinear in this region. The disc in Experiment III was post-cured/degraded at higher temperatures than that in Experiment II. While the weight loss measurements of Experiment III indicated that some degradation had occurred, the maximum value of tan δ in the α-loss region appeared to indicate that the disc was more fully cured than that of Experiment II. This is possible since cure and degradation reactions may occur simultaneously at a high enough temperature. The α-loss regions for the discs of Experiments IV and V, which were increasingly degraded specimens, were shifted to lower temperatures as predicted.

It will be shown later (F.7.c) that the dehydration of the network which, to a large extent, preceeds further degradation by network scission, gives rise to aliphatic double bonds in the network structure (structures VI and VII). This causes a stiffening of the aliphatic portion of the network and is accompanied by a corresponding shift in the glass transition to higher temperatures. The fact that increasingly degraded specimens showed a shift of the α-loss region to lower temperatures confirms that appreciable scission must have occurred since the effects of this were greater than the combined efforts of further cross-linking/cure reactions and the dehydration reaction.

As pointed out earlier, the results for this temperature region were only a qualitative guide to the properties of the discs. The time scale of the measurement of the dielectric properties was such

that some slight degradation must have occurred during measurements at the higher temperatures.

The dielectric results served to characterise the effects of degradation on the physical properties of the resin network. The interpretation of the results is consistent with the reaction schemes which are proposed for the degradation on the basis of the analytical results and which summarise the chemical processes occurring during degradation. The macroscopic physical properties of the resin both before and after degradation are thus related to its chemical structure and to changes in its chemical structure which accompany degradation.

The analytical results alone show that attempts to explain the mechanism of degradation on the basis of reactions of unreacted monomeric resin which have been made by some workers (Neiman, Kovarskaya, Golubenkova, Strizhkova, Levantovskaya and Akutin[45]) are unrealistic. The dielectric results provide ample confirmation.

The dielectric results have a bearing on the practical use of this resin hardener system. It is clear that a post-cure at a temperature of 240°C under conditions which prevent oxidation will produce a material which will retain good electrical and mechanical properties at temperatures up to 200°C providing oxidation, which is appreciable above 180°C, is prevented.

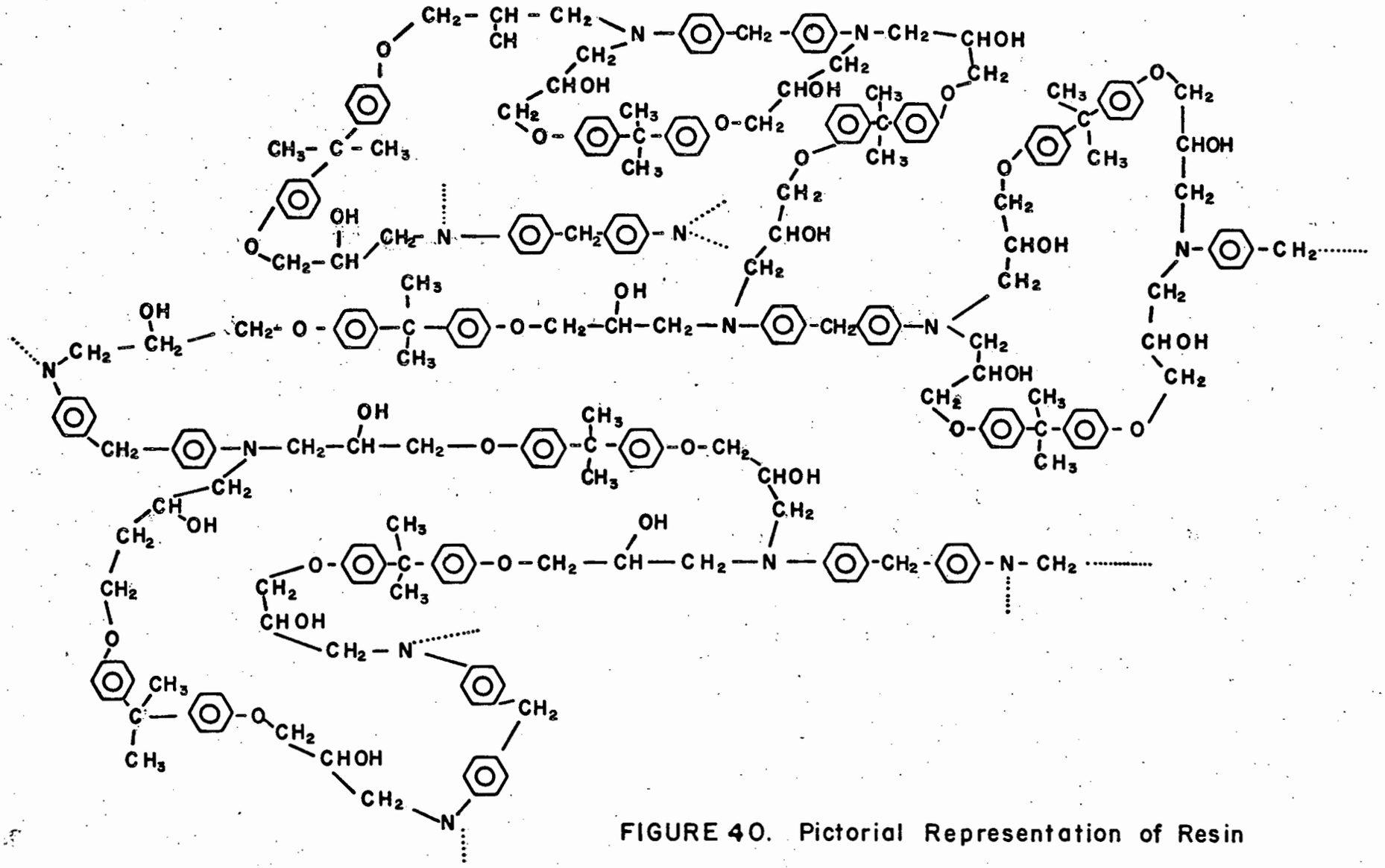
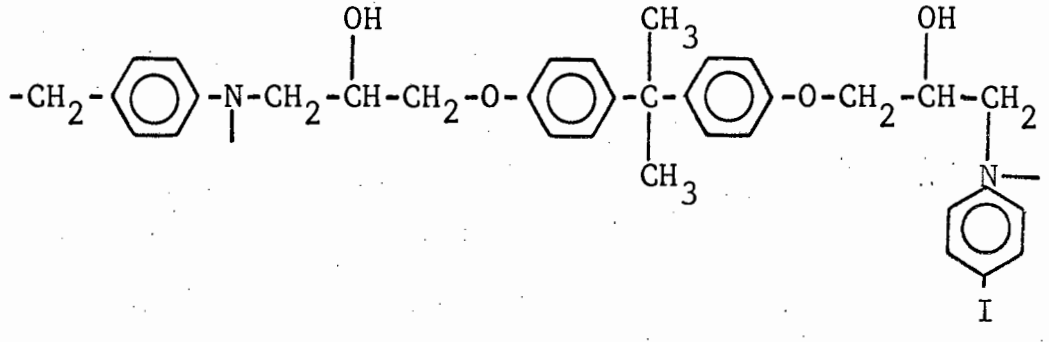


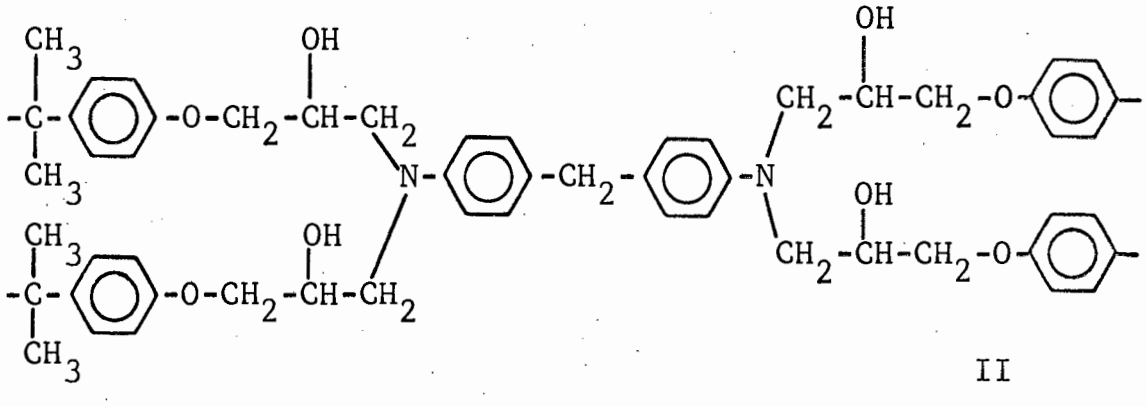
FIGURE 40. Pictorial Representation of Resin Structure.

F.4: The initial structure of the resin

Ideally, the structure of the resin before degradation can be represented by the following formulae:

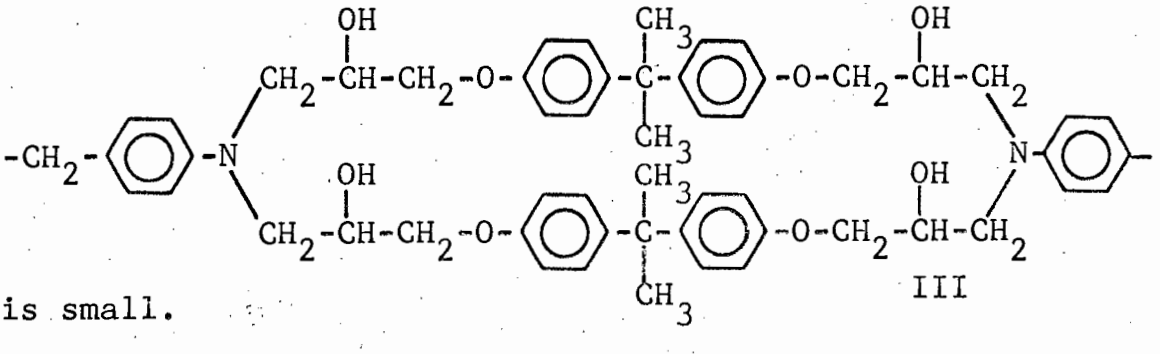


I



II

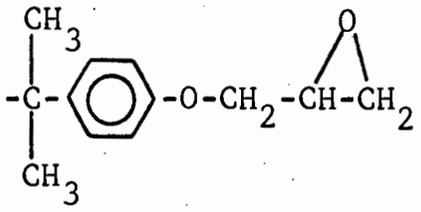
Figure 40 gives a pictorial representation of the whole structure. Such a structure, by virtue of the tetrafunctionality of the diamino residue and the difunctionality of the Bisphenol A residue, is highly cross-linked. As discussed previously under Cure (section F.2.) the structure is completely random so that the cured resin is amorphous. The number of pairs of Bisphenol A residues joined by the same nitrogen atoms:



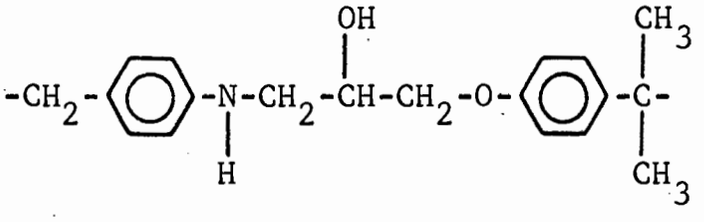
III

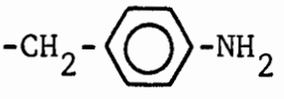
is small.

In fact the ideal, fully-cured structure is never realised. In addition to the above structure (I and II) some unreacted epoxide 'ends':



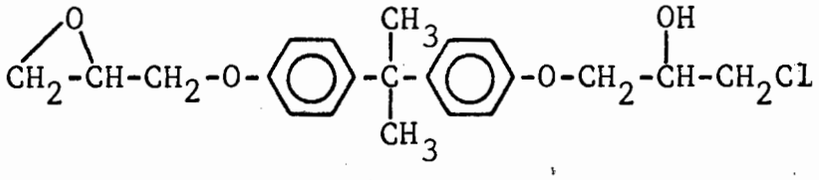
together with some secondary amine and primary amine groups:





will exist in the network before degradation. The percentage of such structures is, however, small as has been discussed (section F.2).

In addition to these structures, because of impurities in the original diglycidylether of Bisphenol A, there will be some unreacted 'ends' , because of the presence of molecules with the structure



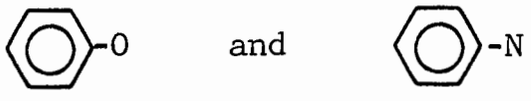
in the uncured resin . Furthermore, as pointed out in the description of the starting materials (section D.I.1) some 1 - 2% of the diglycidylether of Bisphenol A has 2,4' substitution instead of 4,4'. The percentage of these impurities in the cured resin is small.

In view of the small quantity of impurities and the relative completeness of the cure it is reasonable to limit the discussion of the degradation to a discussion of the idealised structure (I and II). References to the other non-ideal structures will be made when necessary.

F.5: The strengths of the chemical bonds in the idealised network

Keenan[32,33] examined the structure of the idealised network (I and II) and came to the following conclusions:

(i) The strongest bonds in the network are the aryl-oxygen and aryl-nitrogen with the former the stronger of the two:



(ii) The remaining bonds were classified in order of decreasing bond strengths as follows:

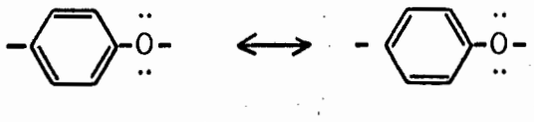
$$C\text{-}H > C\text{-}O > H_2C\text{-}\emptyset > C\text{-}C > (CH_3)_2C\text{-}\emptyset > C\text{-}N$$

where $\emptyset$ denotes aryl.

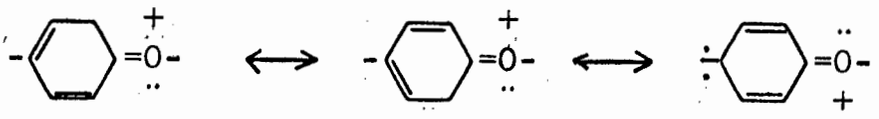
The appearance of phenolic and aryl-amino compounds as major degradation products appears to confirm his first conclusion. Keenan's classification of the strengths of other bonds in the network requires qualification.

F.5.a: The strengths of the aryl-oxygen and aryl-nitrogen bonds

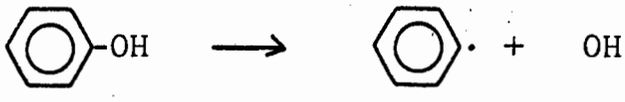
The high stability of these bonds is a result of the contributions of resonating structures. In the case of the aryl-oxygen bond, the electron density between the oxygen and the benzene ring is increased by contributions to the classical structures



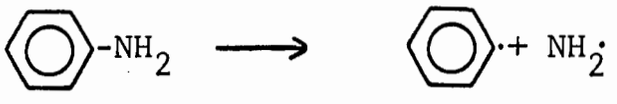
from the structures



The lone pair of electrons on the nitrogen atom, in the case of the aryl-nitrogen bond, contribute similarly to its strength. The stability of these bonds is reflected in values for the dissociation energies of these bonds in phenol and aniline. The reaction



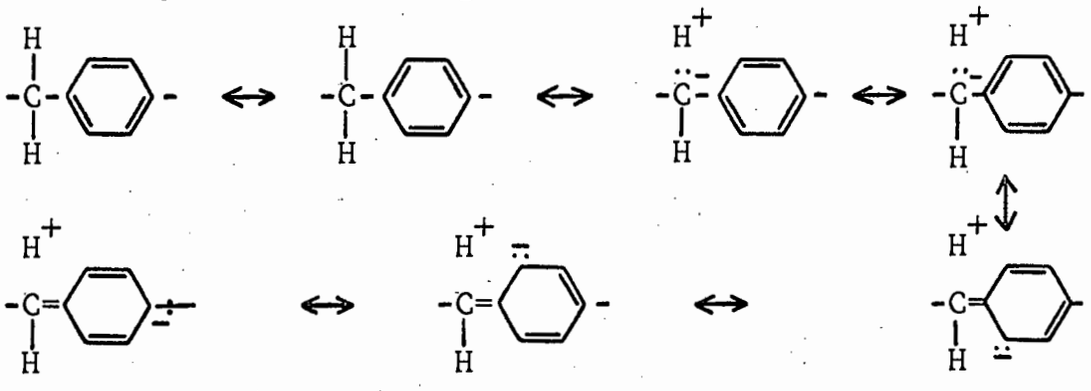
requires 107 k.cals/mole (Semenov[57]) or 96 k.cals/mole (Benson[8]). Despite the discrepancy between these values, they are both high. Similarly the reaction



requires 94 k.cals/mole (Semenov[57]).

F.5.b: <u>The strengths of the aryl-carbon bonds</u>

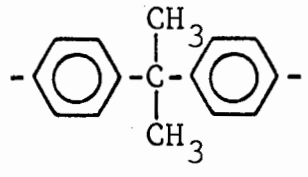
In the structure - CH_2-Ø- hyperconjugative effects lead to the contribution of resonating structures which may tend to strengthen the C - Ø bond:



Such structures tend to increase the electron density of the benzene ring. The presence of an oxygen or nitrogen atom para- to the aliphatic carbon decreases the effectiveness of hyperconjugation since, as detailed above, migration of the lone pair of electrons available on these atoms also give rise to resonating structures whose effect is to increase the electron density of the benzene ring. Such effects, therefore, oppose each other. Semenov[57] quotes a value of 76.5 k.cals/mole for the energy required by the reaction

$$C_6H_5\text{-}CH_2\text{-}C_6H_5 \longrightarrow C_6H_5CH_2^{\cdot} + C_6H_5^{\cdot}$$

The bond dissociation energy of the CH_2-Ø bond in the structure is therefore likely to be less than 76.5 k.cals/mole so that it is weak.

In the structure  hyperconjugative effects which lead to an increased electron density on the benzene ring are no longer possible. Because of this and because of the crowding effects of the relatively bulky methyl groups the

$(CH_3)_2C$-Ø

bond is likely to be weaker than the

CH_2-Ø

bond and is probably one of the weakest bonds in the resin structure.

F.5.c: The strengths of the other bonds in the network

Aliphatic carbon-oxygen bonds tend to be stable. For example, Semenov[57] quotes a value of 90 k.cals/mole for the dissociation of ethanol:

$$C_2H_5OH \longrightarrow C_2H_5\cdot + OH\cdot$$

While stable bonds, they are not however likely to be as stable as aryl-oxygen bonds for reasons discussed in section F.5.a.

The strengths of the remaining aliphatic carbon-carbon and carbon-nitrogen bonds appear to be comparable. The standard bond dissociation energy of an aliphatic carbon-carbon bond is 80 k.cals/mole. In the resin structure, the presence of the neighbouring electronegative oxygen and nitrogen atoms in the unit

$$-O-CH_2-\underset{\displaystyle OH}{\underset{|}{C}}H-CH_2-N-$$

may tend to decrease the aliphatic carbon-carbon bond strengths. For the dissociation

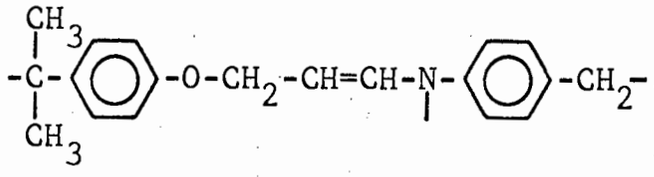
$$CH_3NH_2 \longrightarrow CH_3^{\cdot} + NH_2^{\cdot}$$

Semenov[57] quotes a value of 79 k.cals/mole. The bond dissociation energy of the aliphatic carbon-nitrogen bond in the resin structure is likely to be of this order and hence comparable with those of the aliphatic carbon-carbon bonds.

F.5.d: Bond strengths in the dehydrated idealised resin structure

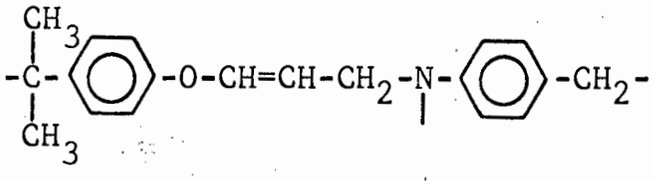
As will be discussed in detail in section F.7.c., a dehydration reaction is the major degradative process occurring during pyrolysis of the resin. This reaction changes the structure of the resin network and it is

necessary to examine the bond strengths in the dehydrated structure. The dehydration reaction leads mainly to the following structures in which elimination of water from the aliphatic portion of the chain has occurred principally in two ways:



IV

and

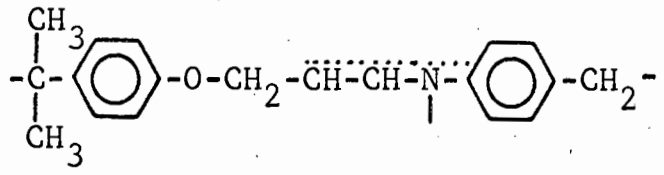


V

The strengths of the carbon-carbon bonds in the aliphatic portion of the chains are now radically altered.

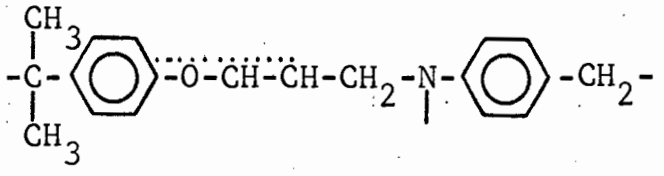
In the structure IV the existence of a double bond adjacent to the nitrogen atom may lead to a pseudo-conjugated system resulting in a considerable strengthening of the bonds involved. A resonance structure with contributions from the following structures:

together with contributions from structures in which there is conjugation of the nitrogen atom with the benzene ring as described in section F.5.a. exists. This leads to a structure which shows extended delocalisation and which may be represented by the formula:



VI

The structure V for similar reasons may be represented by the formula:



VII

It is clear that the bonds involved in the delocalisation are considerably stabilised. The strengths of the remaining non-conjugated bonds (in the case of VI the aliphatic carbon-carbon and carbon-oxygen bonds and, in the case of VII, the aliphatic carbon-carbon and carbon-nitrogen bonds), are changed from those in the original resin network.

The dissociations

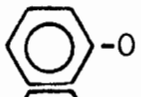
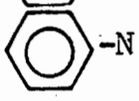
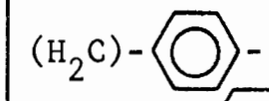
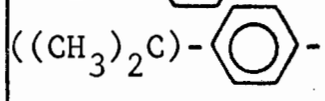
$CH_2 = CH - CH_2 - OH \longrightarrow CH_2 = CH - CH_2^{\cdot} + OH^{\cdot}$

and

$CH_2 = CH - CH_3 \longrightarrow CH_2 = CH^{\cdot} + CH_3^{\cdot}$ require 71 k.cals/mole and 90 k.cals/mole respectively (Semenov[57]). The bond dissociation energies of the carbon-oxygen and the carbon-carbon bonds in structure VI may be expected to parallel these values so that the former bond is considerably weakened while the latter is strengthened. A parallel situation occurs in structure VII.

Table 7 lists the bonds present in the idealised fully cured and dehydrated resin structures in order of decreasing bond strengths together with estimates of bond dissociation energies.

Table 7

Bond	Estimated Bond Dissociation Energy k.cals/mole
	100
	95
(CH=CH)-O and (CH=CH)-N	>90
(CH=CH)-C	90
C-O	90
C-C and C-N	80
	<76.5 a
	<a
(CH=CH-H_2C)-O	70
(CH=CH-H_2C)-N	65

F.6: The mode of energy transfer between bonds

A highly cross-linked resin is, by virtue of its theoretically infinite molecular weight, infusible. Because of this, it stands in a class of its own when modes of energy transfer between bonds are considered. In gases and liquids energy is transferred by collisions between molecules. The total energy of any particular molecule is distributed amongst all possible degrees of freedom more or less according to the Principle of Equipartition of Energy. In a cross-linked resin at temperatures below the glass transition temperature, segmental motion, which involves rotation about single bonds is precluded. Energy transfer by collisions of parts of the network with neighbouring parts cannot occur. Above the glass transition temperature, segmental motion is possible and it is possible to consider energy transfer between neighbouring portions of the network by collisions. During degradation the resin is above its glass transition temperature as described in section F.3. Throughout the degradation the resin remains, however, a solid in which movement of any particular part of the network molecule relative to neighbouring parts is severely hindered. This is so, since, because of the resins highly cross-linked structure, only co-ordinated segmental motion is possible such that the movement does not perturb other parts of the network. If scission of bonds in the network occurs, the free ends so produced may move more easily. It is for this reason that the discussion of degradation of the network will be limited largely to a discussion of the most probably scissioned chemical bonds and to how the subsequent reactions of the free ends produced lead to degradation products.

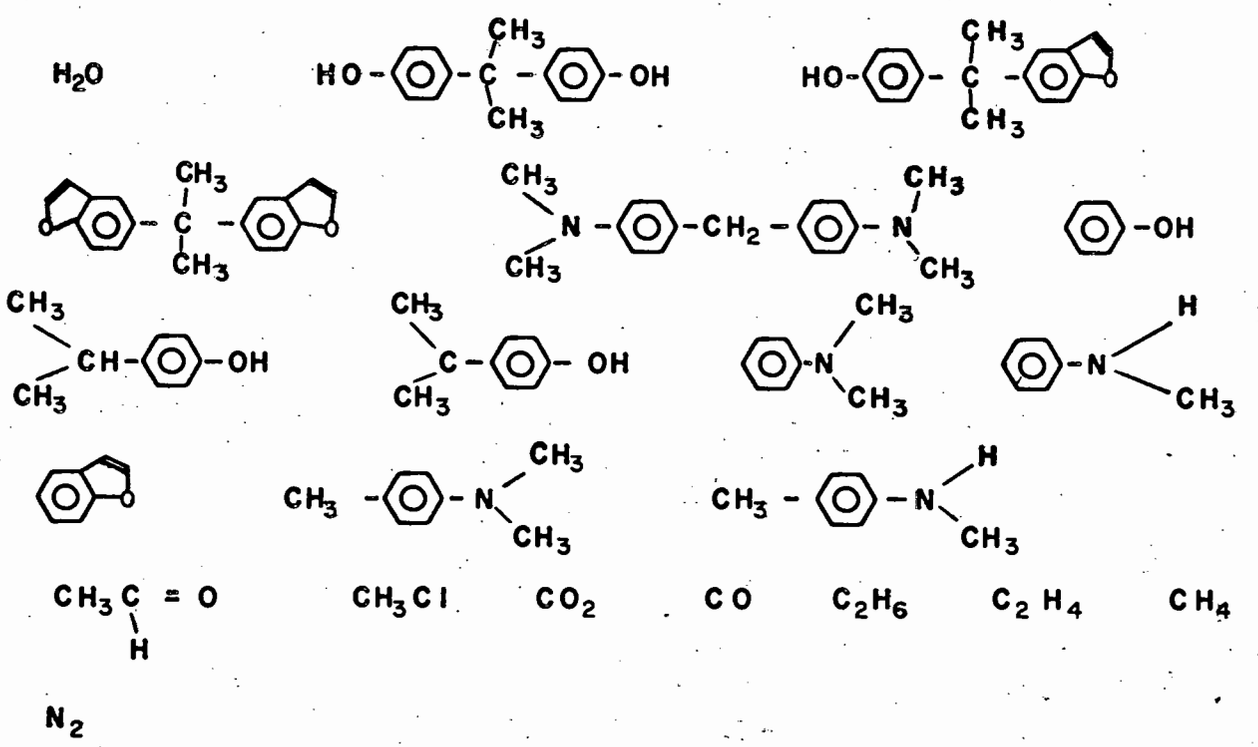


FIGURE 41: Chemical Formulae of Degradation Products.

F.7: Degradation mechanisms

F.7.a: Degradation products

The major condensible degradation products together with the gaseous degradation products are tabulated in table 6 (section E.II.5). The chemical structures of these products are collected in figure 41.

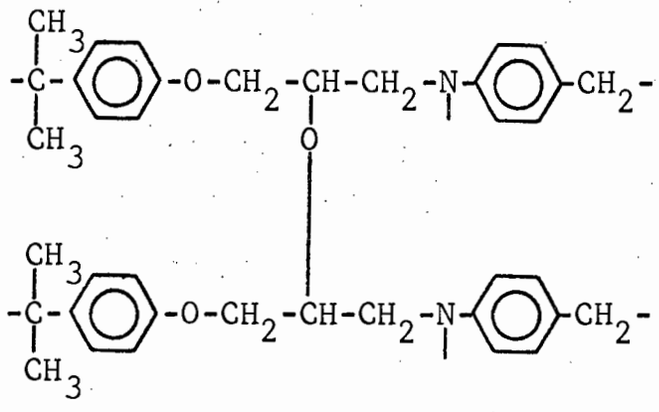
F.7.b: Nature of the degradation processes

Water is the major degradation product. Because of the strength of the aryl-oxygen bond, it is not reasonable to consider its formation from this part of the resin structure but rather from the hydroxyl group in the aliphatic portion of the chain. As will be explained in detail below its formation does not involve a breakdown of the network structure in that no chains are broken, although, as described earlier, the consequential formation of a double bond leads to a stiffening of the resin network (section F.3). The formation of the other major degradation products must, because of their chemical nature, involve a breakdown of the network by the scission of chemical bonds. The question arises as to whether this scission occurs by a homolytic process resulting in free radicals or by a heterolytic process producing ions. In the absence of agents in the resin which could act catalytically to initiate heterolytic fission, it is more reasonable to formulate the degradative processes as occuring by homolytic scission because in general such a process requires less energy than heterolytic fission. In fact, there is evidence[26,30] that free radicals do exist in the degraded resin and in the tarry products of degradation.

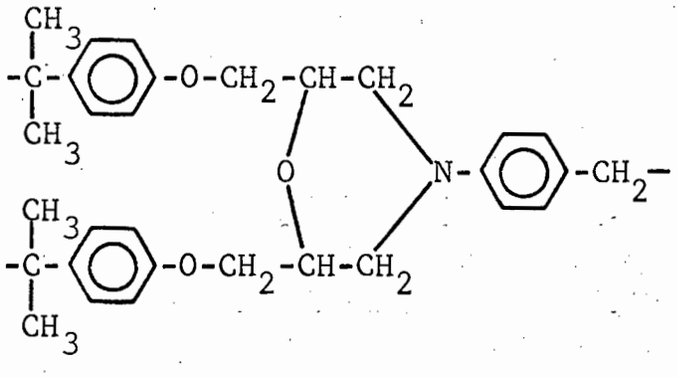
F.7.c: The dehydration reaction

Considerable quantities of water are formed during degradation. Analysis indicated that some 65% of all the available hydroxyl groups were converted to water.

Without anticipating the mechanism of the process it is clear that it involves removal from the network of a hydroxyl group and a hydrogen atom which combine to form water. This can occur in several ways. Elimination of the hydroxyl group together with a hydrogen atom from the adjacent carbon atom can lead to structures VI and VII (section F.5.d). It is possible that water may be eliminated from two hydroxyl groups in adjacent chains to form an ether bridge:



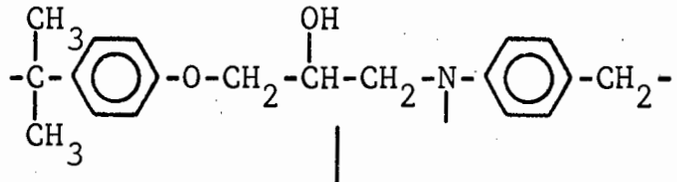
In the case where the aliphatic portions of the chains are joined to the same nitrogen atom, a morpholine type structure is produced:

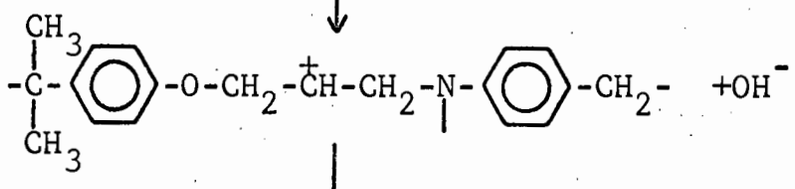


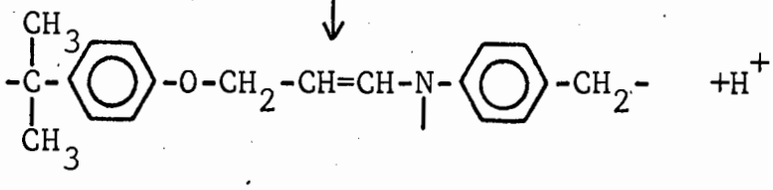
In the case of the removal of a hydroxyl radical from the chains, free radical structures may be left

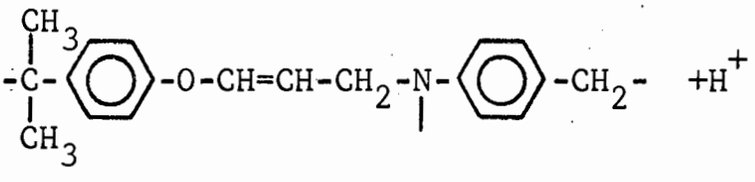
in the network.

There are three distinct possible mechanisms for the formation of water. The first, an ionic mechanism, is not considered likely because in the absence of agents in the resin likely to catalyse the reaction, the formation of ionic species requires high energy. The process would involve loss of a hydroxyl ion to form a carbonium ion which would stabilise by eliminating a proton, combination of hydroxyl ion and proton producing water:

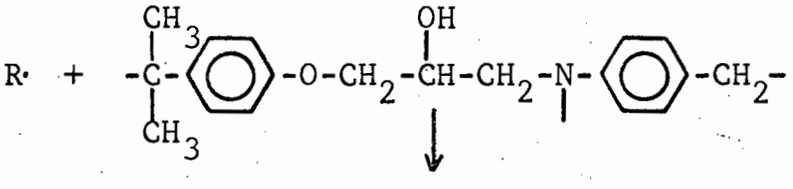
e.g. 

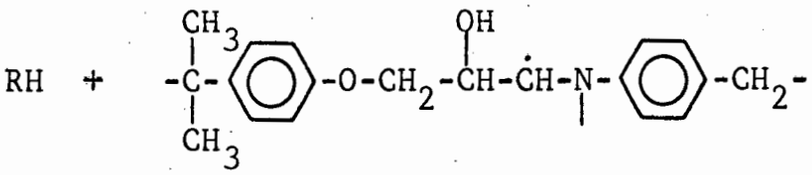




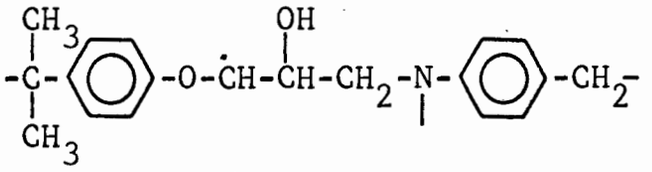
or 

The second possible mechanism involves free radical formation. In this case two possible mechanisms are possible. The first assumes the existence of an unspecified radical in the network which abstracts a hydrogen atom from the aliphatic portion of the chain.

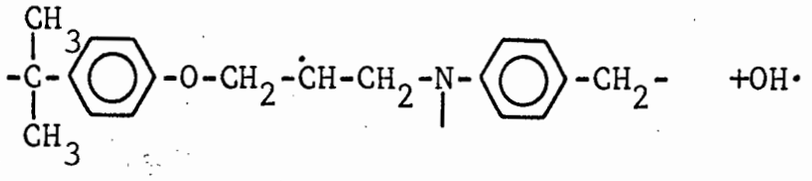




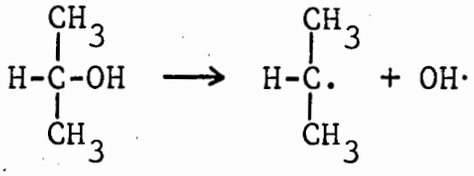
or



followed by elimination of a hydroxyl radical from the free radicals so formed to produce double bonds. The hydroxyl radical abstracts hydrogen from an unspecified part of an aliphatic chain to produce water. Secondly, it is possible that a hydroxyl radical is produced from the chain:



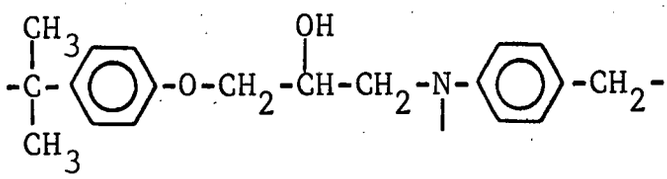
This abstracts hydrogen from an aliphatic chain to produce water. Both reactions are possible but a serious objection to both is that they involve scission of a carbon-oxygen bond which is of relatively high stability. The dissociation



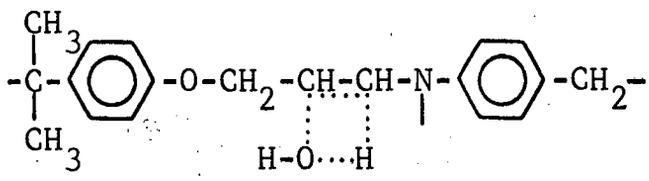
requires some 90 k.cals/mole (Semenov[57]) and it is reasonable that the parallel reaction in the network will require similar energy. This is greater by some 10 k.cals/mole than the energy required tosplit an aliphatic carbon-carbon bond or carbon-nitrogen bond. The loss of a hydroxyl radical from the network is therefore not likely.

In view of the objections to the above schemes,

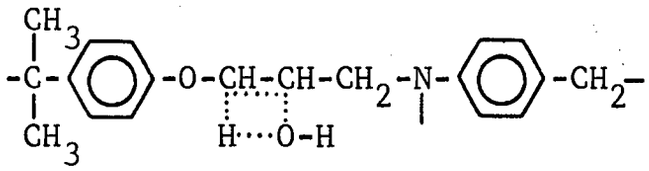
the most probable reaction to form water is a molecular reaction in which water is released from the unit:



via a transition state:



or



which breaks down to form water and the olefinic structures VI or VII. Elimination of water from two adjacent hydroxyl groups to form an ether bridge may be expected to occur similarly. Semenov[57] has given a detailed discussion of a similar reaction viz. the decomposition of alkyl bromides which can occur either by a free radical mechanism or a molecular decomposition, the major mode depending on the structure of the molecule and reaction conditions.

For the dehydration of the resin, the molecular decomposition is to be preferred as the radical mechanism requires high energy. In addition, the formation of other degradation products is easily explained from the structures VI and VII. The formation of ether bridges by elimination of water from neighbouring hydroxyl groups is not likely to occur to a great extent. In this case, the objection to the reaction is not on the grounds of the energies involved but arises from the fact that the number of

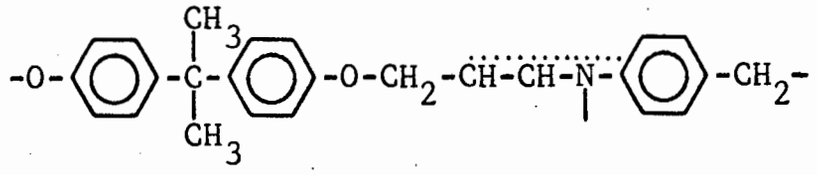
pairs of hydroxyl groups which at any instant may be near enough to react is very small. This is true because of the random nature of the resin network which has been discussed earlier. (section F.1.). The formation of the olefinic structures VI and VII (section F.5.d) is, therefore, the predominant process accompanying the formation of water. The dehydration reaction appears to precede further degradation of the resin. Evidence to support this is to be found firstly from the quantity of water found and secondly in that the formation of the second most preponderant degradation products namely the phenolic compounds, is only readily explicable from the structure VI and not from the original structure I and II, as described in section F.7.e.

F.7.d: Scission of network bonds

The scission of any chemical bond in the network may be followed by several processes each of which may lead to the stabilisation of the two free radicals produced. The most probable process is simply recombination to reform the original bond so that, in the absence of any other stabilisation processes, at any temperature an equilibrium would be set up in which the number of free radicals existing at any instant would be constant. The occurrence of other possible processes precludes the existence of any equilibrium and it is by means of these processes that the resin network is broken down. The breakdown of the network is marked by the appearance of small fragments of the network. These fragments which are formed by processes accompanying the stabilisation of radical free ends other than by recombination, constitute the major degradation products other than water.

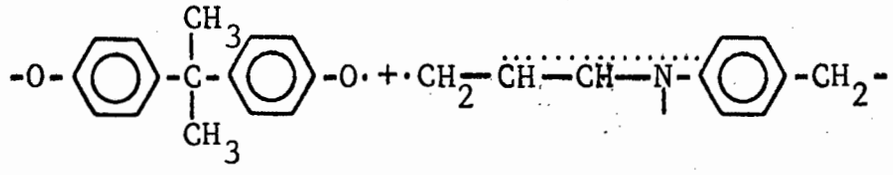
F.7.e: Formation of phenolic degradation products

It has been established that, following the initial dehydration reaction, the structure

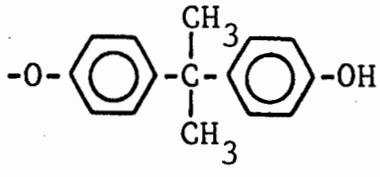


VI

exists in large proportion in the resin network. The aliphatic carbon-oxygen bond is now a weak one and may scission:



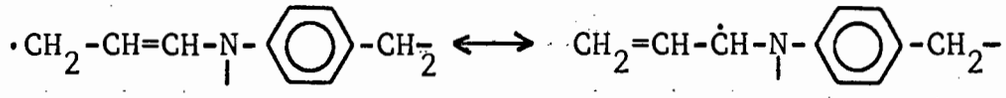
The first radical may abstract hydrogen from a neighbouring chain to form a phenolic free end:



Abstraction of radicals other than hydrogen (such as methyl) is unlikely since

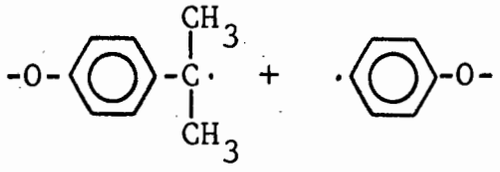
(i) there are relatively few such radicals and
(ii) such a process is not favoured energetically (Semenov[57]).

The remaining radical is appreciably stabilised by resonance.

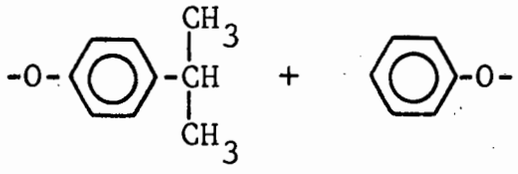


The successive scission of two aliphatic carbon-oxygen bonds adjacent to one diphenylpropane residue followed by hydrogen abstraction leads to the formation of Bisphenol A.

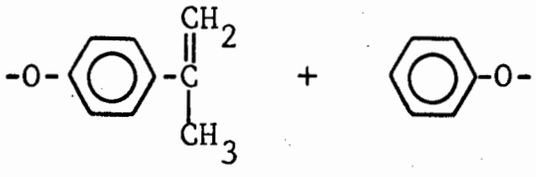
The formation of phenol, p-isopropylphenol and p-isopropenylphenol require the scission of the isopropyl-aryl bond. This is a relatively weak bond. Scission of the bond to produce the free radicals



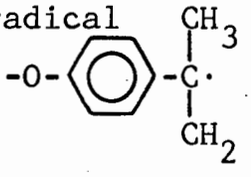
may be followed by hydrogen abstraction from neighbouring chains by the radicals to form

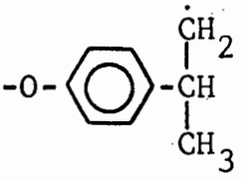


or by disproportionation to form

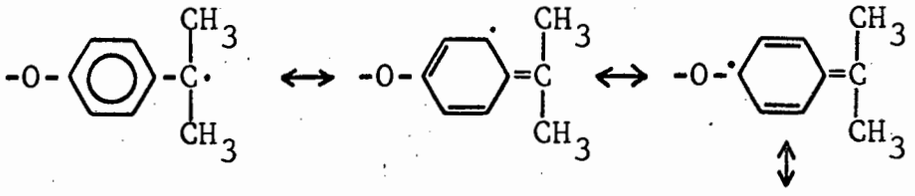


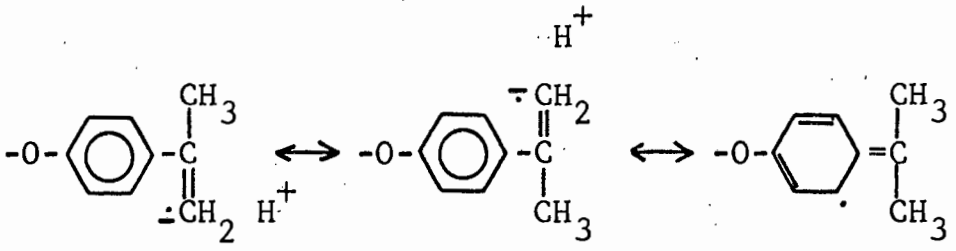
which is equivalent to hydrogen abstraction by the phenyl radical of a hydrogen atom on the isopropylradical

The radical  is unlikely to isomerise to



since the tertiary radical is more stable. In fact it is stabilised by resonance with the benzene ring and by hyper-conjugative effects:

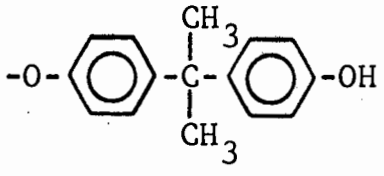




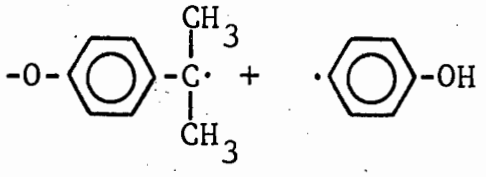
The phenyl radical is not stabilised by resonance and is likely to be more reactive.

The production of phenol, p-isopropylphenol and p-isopropenylphenol are now explained on the basis of the above reactions.

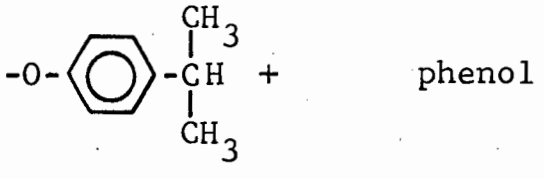
A phenolic free end is formed as described above:



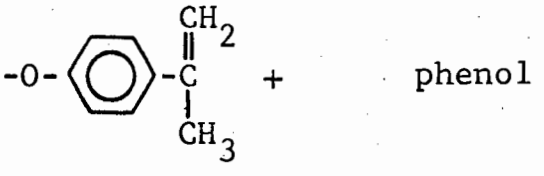
Scission of the isopropyl-aryl bond occurs:



followed either by hydrogen abstraction from a neighbouring chain

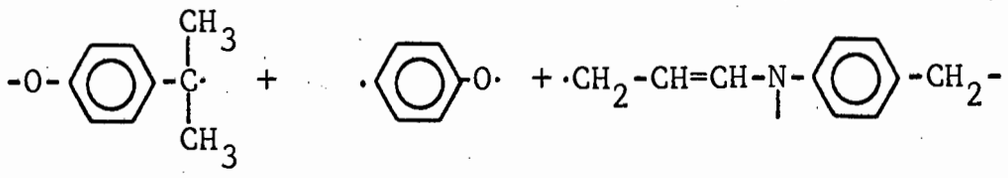


or by disproportionation:

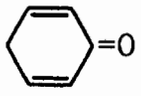


Scission of the remaining allylic-oxygen bond followed by hydrogen abstraction leads to p-isopropylphenol or p-isopropenylphenol. In fact the order of the scissions is not important. What is evident is that stabilisation of the free radicals formed in one scission precedes the other scissions since the

simultaneous scission of two bonds e.g.



would lead to semi-quinoid structures e.g.



which were not present unless in very small quantities.

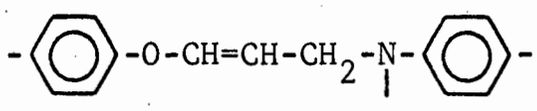
The production of the phenolic compounds identified cannot be reasonably formulated as occuring from the original resin structure (I and II) since the most likely bonds to break are the aliphatic carbon-carbon and aliphatic carbon-nitrogen bonds and not the aliphatic carbon-oxygen bond which is relatively stable.

F.7.f: Formation of arylamino and benzofuryl products

Large quantities of products containing the aryldimethylamino structure (N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane, N,N-dimethylaniline and N,N-dimethyl-p-toluidine) were formed during degradation of the resin. Smaller quantities of secondary amines (N-methylaniline and N-methyl-p-toluidine) were produced. No products containing the primary amine grouping were identified and certainly none was amongst the major degradation products. The formation of large quantities of products containing the benzofuran nucleus (2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane, 2,2-bis-(benzofur-5-yl)propane and benzofuran itself) appeared to complement the formation of the methylamino compounds.

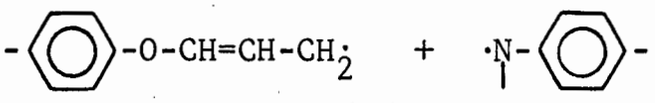
The formation of methylamino compounds from the network before its dehydration is not reasonable. The production of water and of the second most preponderant

species, namely the phenolics, is only readily explicable if dehydration of the network precedes further reaction. In addition the production of the methylamino structure is not feasible from structure VI whose degradation leads to phenolic products (section F.7.e.). These products must, therefore, be produced from structure VII:

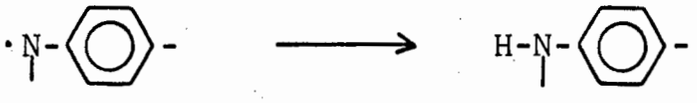


VII

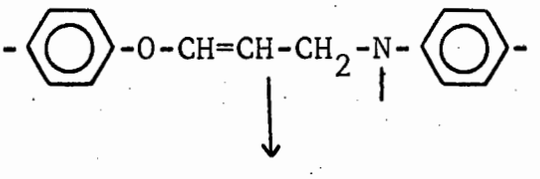
On the basis of the discussion of the production of phenolic compounds from structure VI (section F.7.e), it would be expected that the most likely reaction of structure VII would be scission of the allylic-nitrogen bond to form the free radicals:

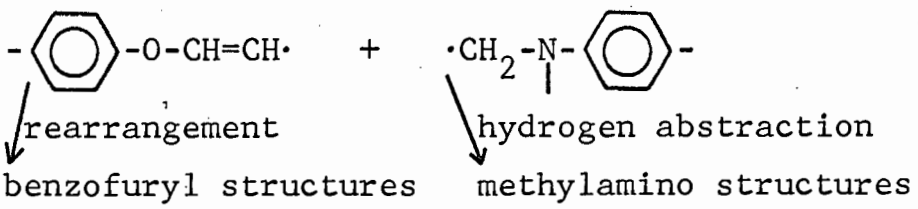


Evidence that this reaction does in fact occur is provided by the formation of the secondary amines by hydrogen abstraction of the radical:

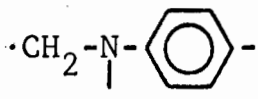


These are not, however, produced in quantities comparable with those of the tertiary amines and nor were any primary amines present amongst the major degradation products. This reaction is, therefore, largely overshadowed by a reaction in which the vinyl-carbon bond scissions:

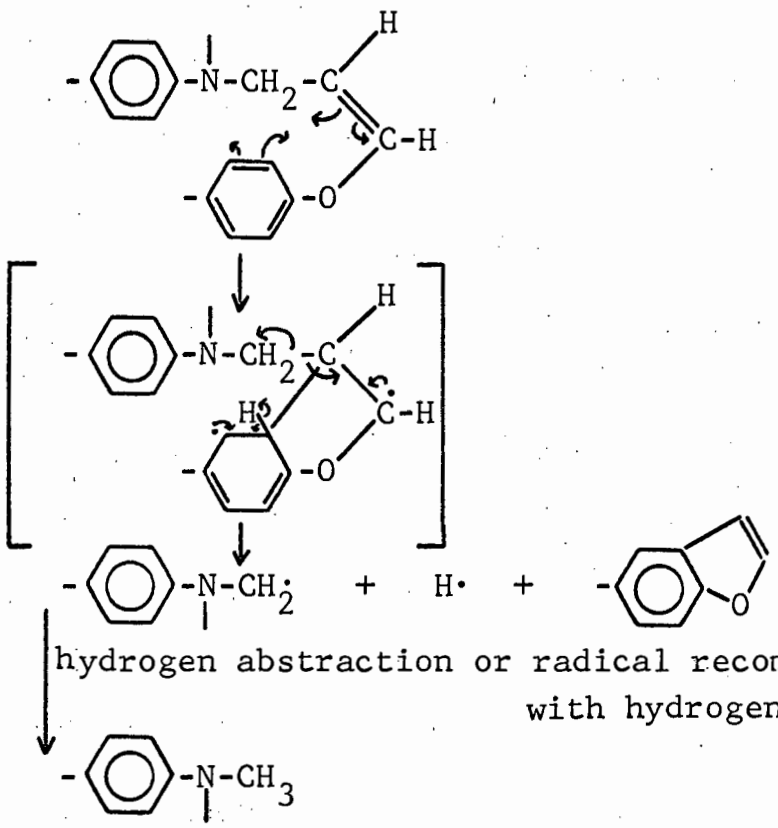




The reaction as formulated above is highly unlikely since the vinyl-carbon bond is much stronger than the allylic-nitrogen bond. The mechanism of the process appears to involve formation of the benzofuran nucleus via a transition state followed by loss of the



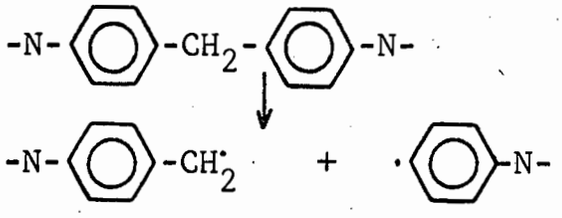
group:



The reason for the preferential formation of the benzofuran nucleus together with the methylamino radical and a hydrogen radical or a methylamino group rather than the scission of the allylic-nitrogen bond is not clear. The explanation may lie in the high stability of the benzofuryl system.

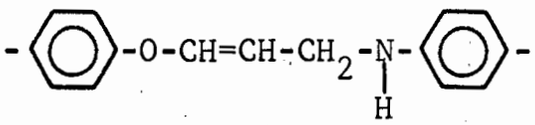
The production of 2,2-bis-(benzofur-5-yl)propane is by the occurrence of two such reactions. 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane is produced by one such reaction together with an allylic-oxygen bond scission (section F.7.3.). The formation of benzofuran requires, in addition to the reaction above, scission of an isopropyl-aryl bond. This has been discussed (section F.7.e.).

The production of N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane is now evident. The formation of dimethylaniline and dimethyl-p-toluidine require the scission of the aryl-methylene bond. The scission:



must be followed by hydrogen abstraction by the radicals produced.

The formation of N-methylaniline and N-methyl-p-toluidine require, in addition to the two reactions outlined above, scission of the allylic-nitrogen bond of structure VII. It is possible that these products might have been produced from a dehydrated partially cured structure in the resin:



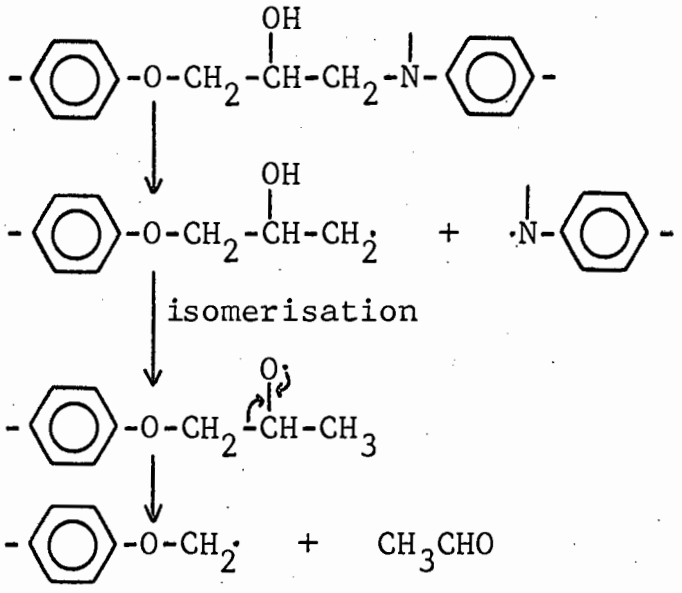
The concentration of such structures in the network is low (section F.2.). Since reasonably large quantities of secondary amines were produced, their production from the dehydrated fully cured structure VII is more likely.

F.7.g: Formation of gaseous degradation products

All these products were minor products of the degradation. Their formation was not related to the formation of the major degradation products and can be regarded as being due to side reactions.

F.7.g.i: Acetaldehyde

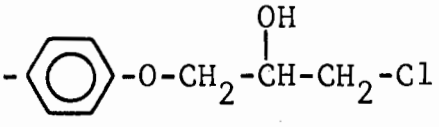
The most reasonable mechanism for the production of acetaldehyde involves scission of the aliphatic carbon-nitrogen bond in the network before the network is dehydrated:



There is evidence for the isomerisation reaction (Semenov[55]). The reaction may give rise to very small quantities of secondary amines and methylphenylethers through hydrogen abstraction by the remaining radicals.

F.7.g.ii: Chloromethane

The cured resin contains 'free ends' (section F.2.)



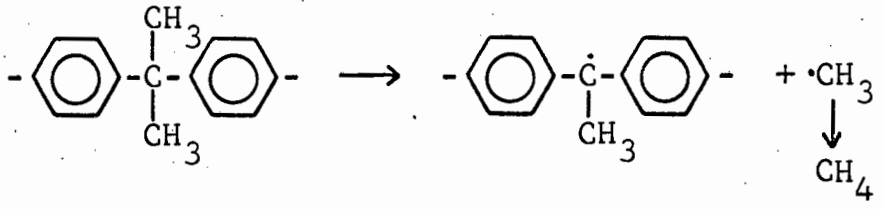
Chloromethane evidently arises from the formation from this species of a chloromethyl radical followed by hydrogen abstraction by this radical.

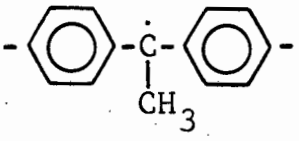
F.7.g.iii: Carbon dioxide and nitrogen

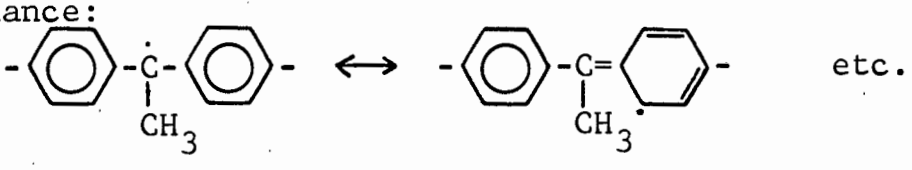
Carbon dioxide is most probably formed as a result of oxidation of the resin during degradation by oxygen from adsorbed air. The traces of nitrogen amongst the degradation products were probably from the same source.

F.7.g.iv: Carbon monoxide, methane, ethane and ethene

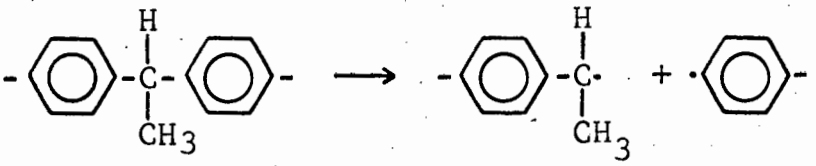
The thermal decomposition of acetaldehyde (Semenov[57]) gives rise to carbon monoxide, methane and small quantities of ethane. The carbon monoxide produced in the degradation probably all arises from the decomposition of acetaldehyde which is the major component of the gaseous degradation products. A percentage of the methane produced also arises in this manner. Methane may also be formed by the loss of a methyl radical from the diphenylpropane nucleus followed by its abstraction of hydrogen:

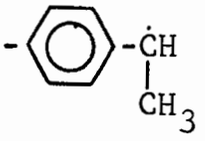


The radical  is stabilised by resonance:

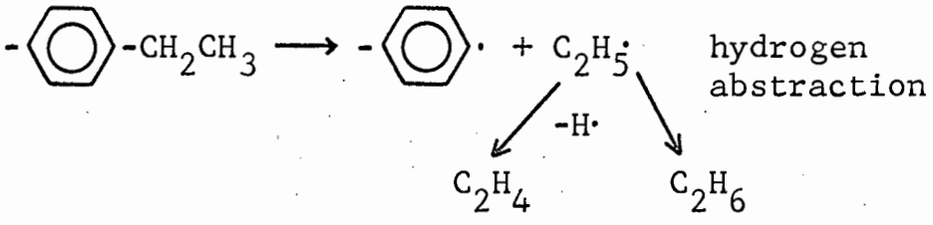


The radical may saturate by abstracting hydrogen from neighbouring portions of the network to form a diphenylethane residue which may further scission:



The radical  may saturate by

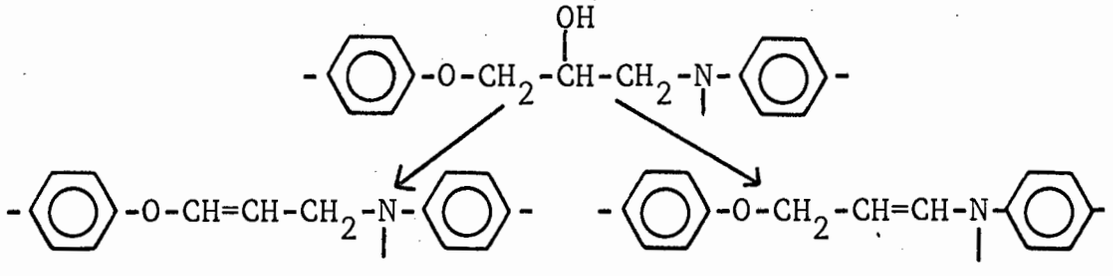
abstraction of hydrogen to form an ethylphenyl structure. A scission of the ethylphenyl bond leads to the formation of the ethyl radical which can either abstract hydrogen to form ethane or lose a hydrogen atom to form ethene:



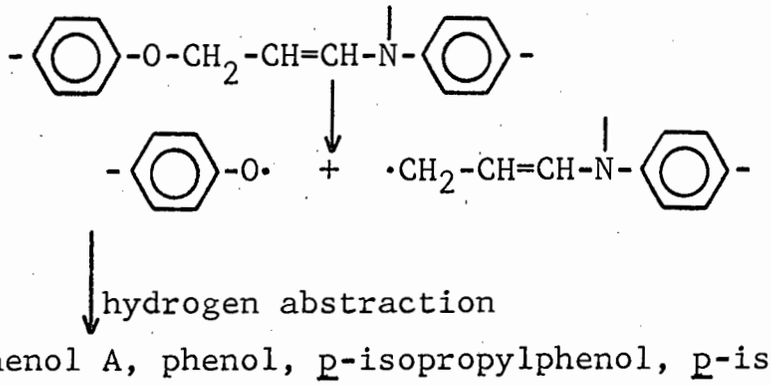
F.7.h: Summary of reaction mechanisms

The reactions described in previous sections are summarised below:

F.7.h.i: Dehydration: (major reaction)

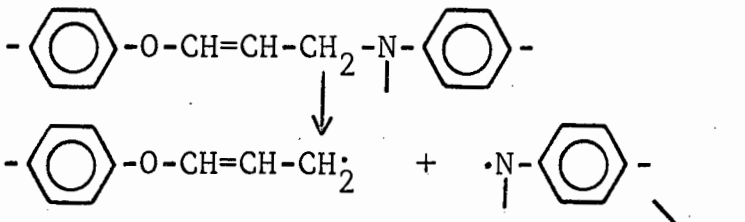


F.7.h.ii: Phenolics (major reaction)



Bisphenol A, phenol, p-isopropylphenol, p-isopropenyl-phenol.

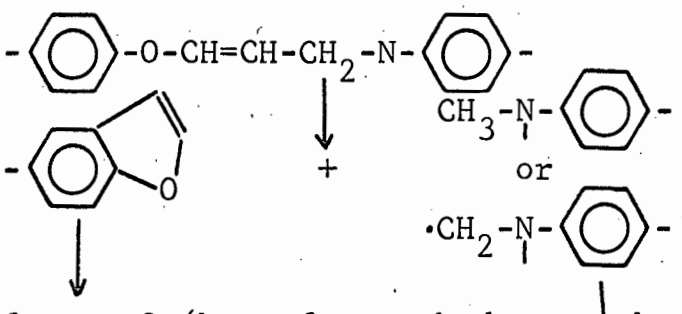
F.7.h.iii: Secondary amines (major reaction)



hydrogen abstraction

N-methylaniline, N-methyl-p-toluidine

F.7.h.iv: Secondary and tertiary amines and benzofuryl structures (major reaction)



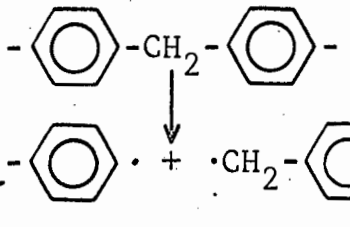
benzofuran, 2-(benzofur-5-yl)-2-(p-hydroxyphenyl) propane

2,2-bis-(benzofur-5-yl) propane

hydrogen abstraction

N,N,N',N'-tetramethyl-p,p'-diaminodiphenylmethane, N,N-dimethylaniline, N-methylaniline, N,N-dimethyl-p-toluidine, N-methyl-p-toluidine

F.7.h.v: Aryl-methylene scission (major reaction)



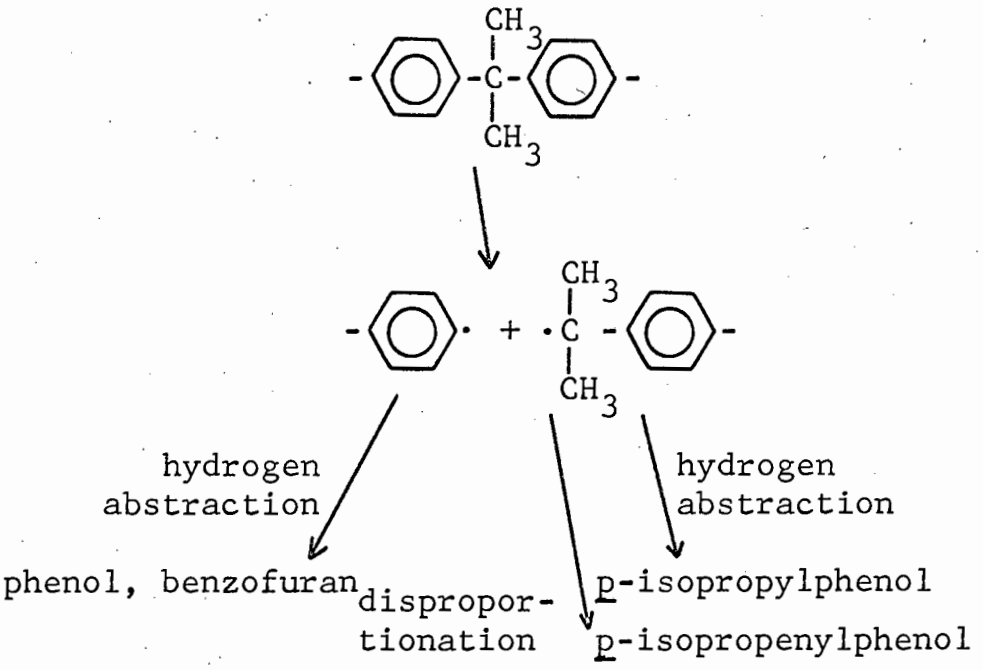
hydrogen abstraction

N,N-dimethylaniline, N-methylaniline

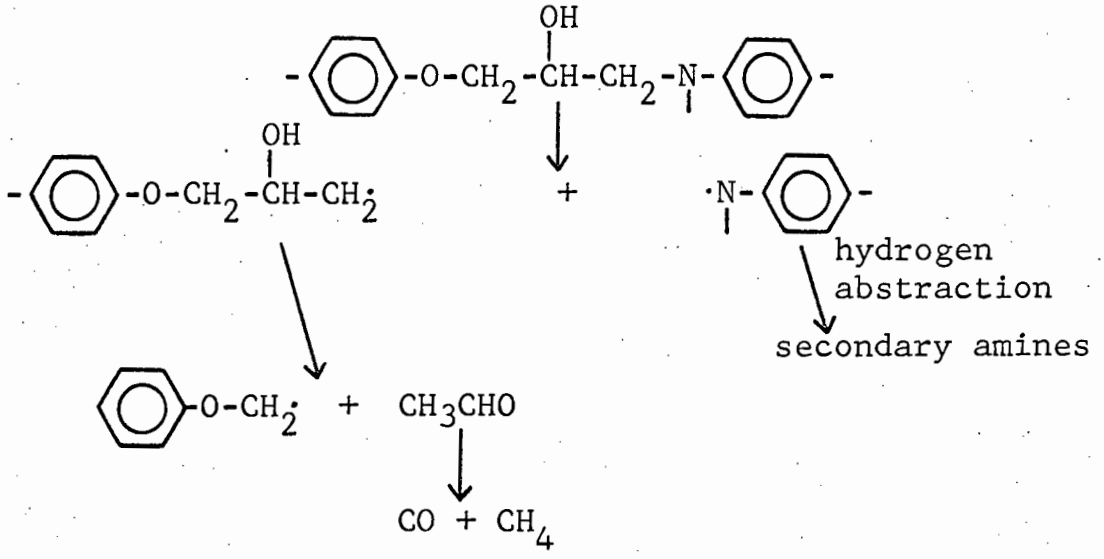
hydrogen abstraction

N,N-dimethyl-p-toluidine, N-methyl-p-toluidine

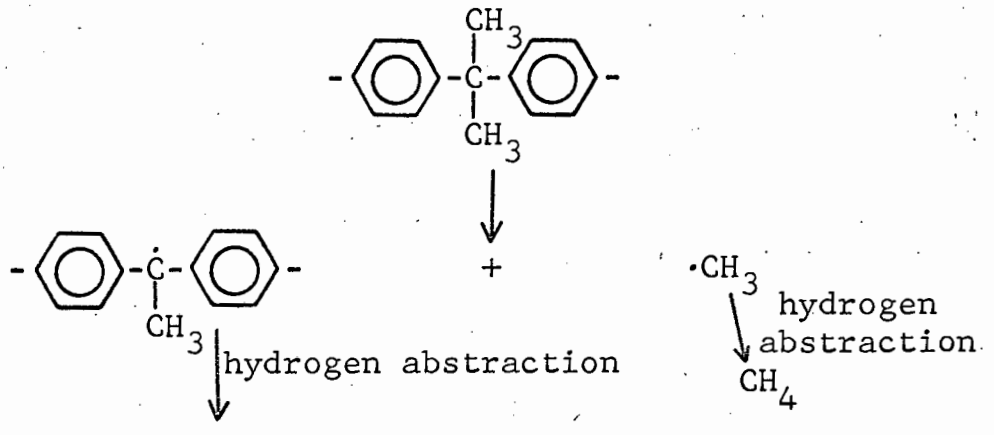
F.7.h.vi: Aryl-isopropyl scission (major reaction)

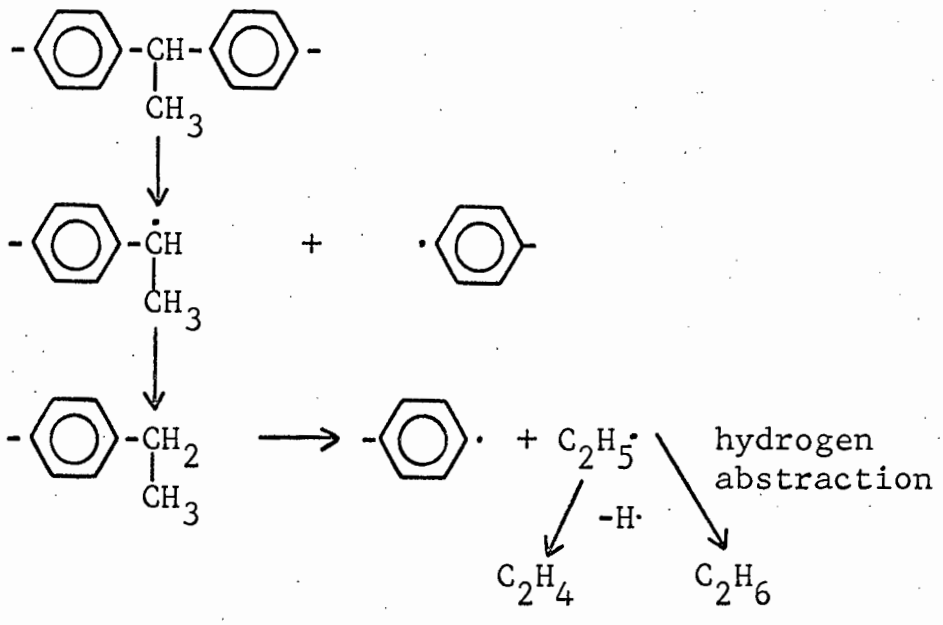


F.7.h.vii: Acetaldehyde formation (minor reaction)



F.7.h.viii: Methane, ethane and ethene formation (minor reaction)





F.7.h.ix: Oxidation (minor reaction)

oxidation $\longrightarrow CO_2$.

F.7.i: Possible reaction products not identified

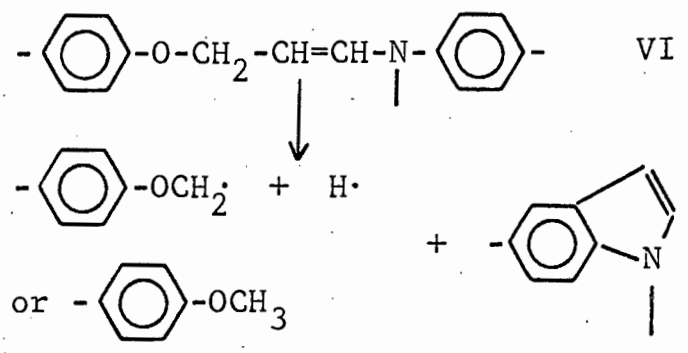
During the course of this work, all the major condensible degradation products as well as the gaseous degradation products were identified (although the use of the word major implies a somewhat arbitrary distinction). In this section an attempt is made, on the basis of the knowledge gained about the degradation, to predict the nature of some of the other products of the degradation.

The formation of benzofuryl structures is accompanied by the possible production of hydrogen atoms (section F.7.f.). The fate of these is either their combination with other radicals present (in particular with themselves to form molecular hydrogen or with the radical $\cdot CH_2\text{-}N\text{-}$) or their saturation by abstraction of hydrogen atoms from the network to produce molecular hydrogen. Radical sites on the network produced in the major degradation reactions

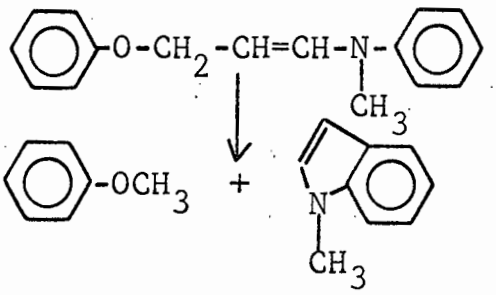
may saturate by combination with atomic hydrogen. A reasonably large quantity of hydrogen would be expected to be produced during degradation. Stuart and Smith[60] who studied the degradation of an aliphatic amine cured Bisphenol A type epoxy resin reported the presence of hydrogen amongst the reaction products as 'highly probable'. Hydrogen was not collected during degradation in this investigation but it is likely that it is a product.

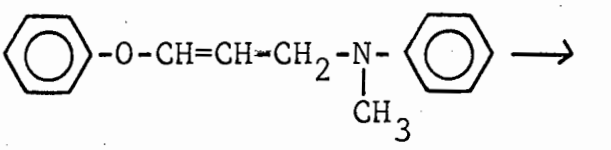
The formation of small quantities of products containing primary amine groups (aniline, p-toluidine, p,p'-diaminodiphenylmethane, N-methyl-p,p'-diaminodiphenylmethane) is possible. The primary amine group would be formed by two allylic-nitrogen bond scissions involving the same nitrogen atom. On the basis of the results obtained, N,N'-dimethyl-p,p'-diaminodiphenylmethane and N,N,N'-trimethyl-p,p'-diaminodiphenylmethane would be expected as degradation products.

An unexpected feature of the reaction is the formation of large quantities of substances containing the benzofuran nucleus. By analogy with the phenolic compounds identified, 5-isopropylbenzofuran and 5-isopropenylbenzofuran are probable products of the degradation. A question which arises from the formation of this series of products concerns the production of substances containing the indole nucleus by an analagous reaction viz.

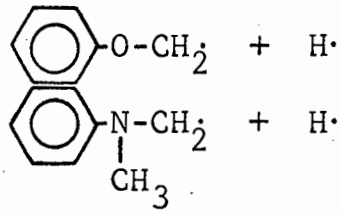


Such substances were not amongst the major products. The reason for the production of large quantities of the benzofuryl series of products as compared with the possible production of only small quantities of products containing the indole nucleus may be found in the stability of the structures involved. To obtain an idea of the stability of these structures, analagous reactions may be considered viz.

(i) 

and (ii)  N,N-dimethylaniline + benzofuran

The reactions are formulated for the sake of the discussion as proceeding to saturated structures. The alternative formation of free radicals (in (i)

and in (ii) )

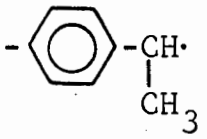
does not, in fact, affect the argument. The heat of formation of N,N-dimethylaniline is greater by some 40 k.cals/mole than that of anisole[27]. Assuming that the stabilities of benzofuran and N-methylindole are comparable, the reason for the production of large quantities of benzofuryl structures during degradation of the resin as compared with the possible formation of only small quantities of indolyl structures is clear. The formation of benzofuryl structures

represents a large increase in stability of the system.

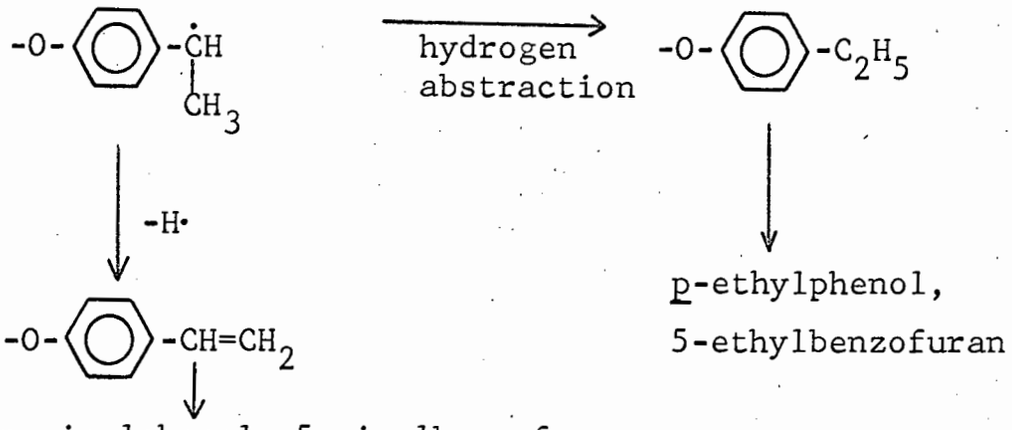
The initial rapid dehydration of the network is an analagous type of reaction. The loss of water from the network which is accompanied by the formation of the olefinic structures VI and VII results in a large increase in stability of the network. This is all the more true as the double bonds formed are conjugated (section F.5.d.).

Compounds containing the indole nucleus may, in fact, be formed in small quantities. The major reactions of the dehydrated structure VI, however, is the expected allylic-oxygen bond scission to yield phenolic products.

In section F.7.g.iv. are outlined the reactions which follow loss of a methyl radical from the diphenylpropane residue and which lead to the formation of ethene and ethane from this part of the network. The formation of the diphenyl ethane nucleus by these means may lead to the production of small quantities of products containing this structure (1,1-bis-(p-hydroxyphenyl)ethane, 1-(benzofur-5-yl)-1-(p-hydroxyphenyl)ethane and 1,1-bis-(benzofur-5-yl)ethane). The formation in the same series of reactions of the radical.

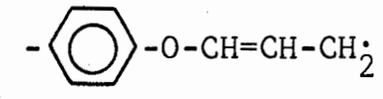


may lead by hydrogen abstraction to the formation of p-ethylphenol and 5-ethylbenzofuran, or, by loss of a hydrogen atom to p-vinylphenol and 5-vinylbenzofuran:

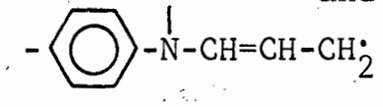


Lee[35] reported the presence of ethyl phenols amongst the products of degradation of a low molecular weight commercial Bisphenol A type epoxy resin cured with p,p'-diaminodiphenylmethane and postulated the formation of vinylphenols amongst these.

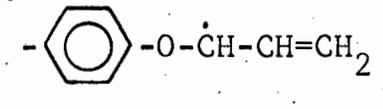
No mention has been made so far of the fate of the propenyl radicals remaining in the network after the formation of phenolic species and of secondary and primary amines: viz.



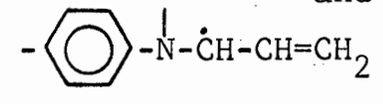
and



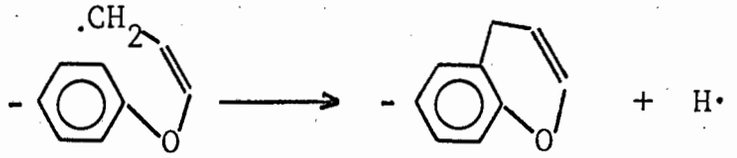
The further reactions of these radicals will depend largely on their stability. A possible fate is combination with other free radical sites in the network. The radicals may abstract hydrogen to form propenylether and propenylamine structures respectively. Alternatively, the radicals may rearrange to the allylic form:

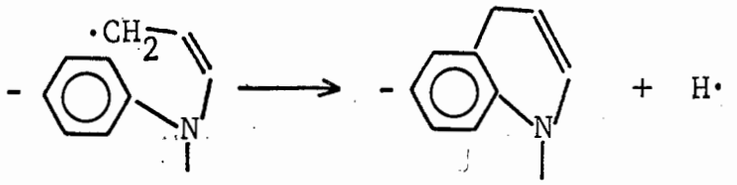


and

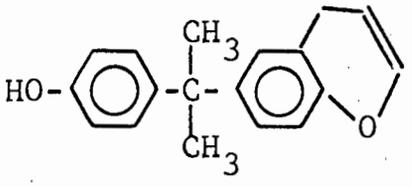


Normally, secondary radicals are more stable than the corresponding primary forms but the presence of the neighbouring electronegative oxygen and nitrogen atoms may oppose the tendency to the rearrangements. Hydrogen abstraction by the allylic forms of these radicals would lead to allylethers and allylamines. The rearrangement of allylphenylethers is well known and facile. The production of o-allylphenolic compounds and p-allylphenol is, therefore, possible. A possible reaction of the propenyl radicals is the formation of benzopyran and dihydroquinoline structures:

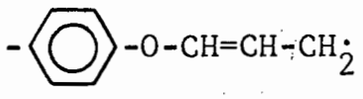




In section E.II.4.m. was discussed the possible presence of 2-(1,4-benzopyran-6-yl)-2-(p-hydroxyphenyl) propane:



as an impurity in the sample of 2,2-bis-(benzofur-5-yl) propane isolated from the degradation products. If this substance was, indeed, the impurity then it may indicate that the most likely reaction of the



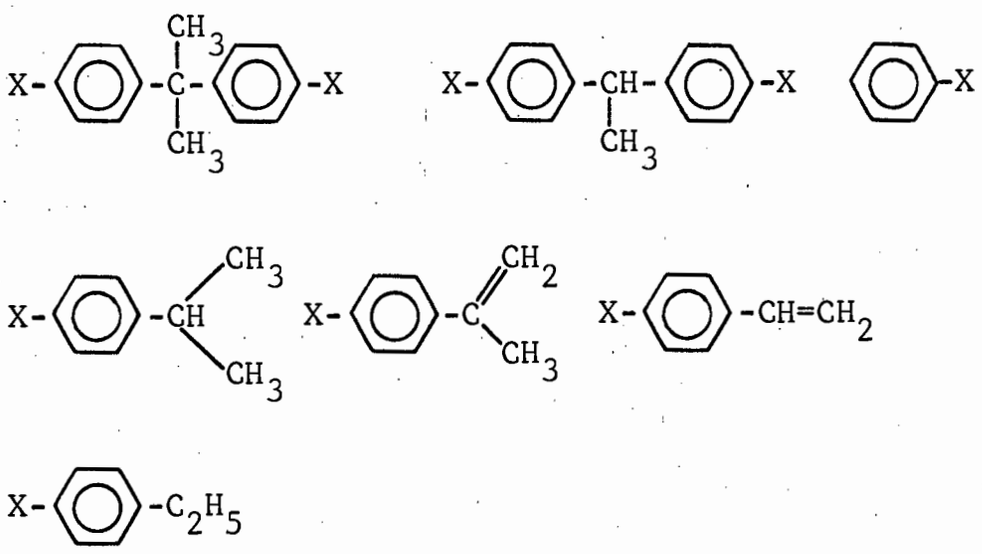
radical is to form 1,4-benzopyranyl structures.

A summary of all possible condensible degradation products is given below. If account is taken of the

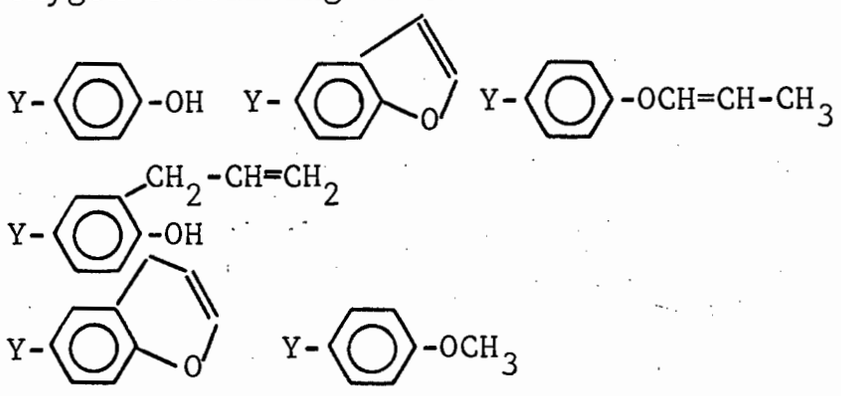
possibility of the formation of products containing the diphenyl propane nucleus to which is attached either similar or different oxygen functions, of products from the diphenyl propane residue containing only one aromatic ring which may be monosubstituted or isopropyl, isopropenyl, ethyl or vinyl substituted and of products containing the diphenyl ethane nucleus to which may be attached similar or different oxygen functions, the reason for the large numbers of minor degradation products is obvious. Similar remarks apply with greater force to the diphenyl methane nucleus because of the trivalency of the nitrogen atoms attached to this nucleus.

(i) Diphenyl propane nucleus:

X denotes an oxygen containing function.

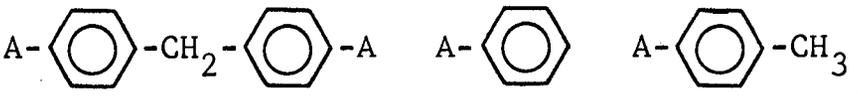


(ii) Oxygen containing functions:

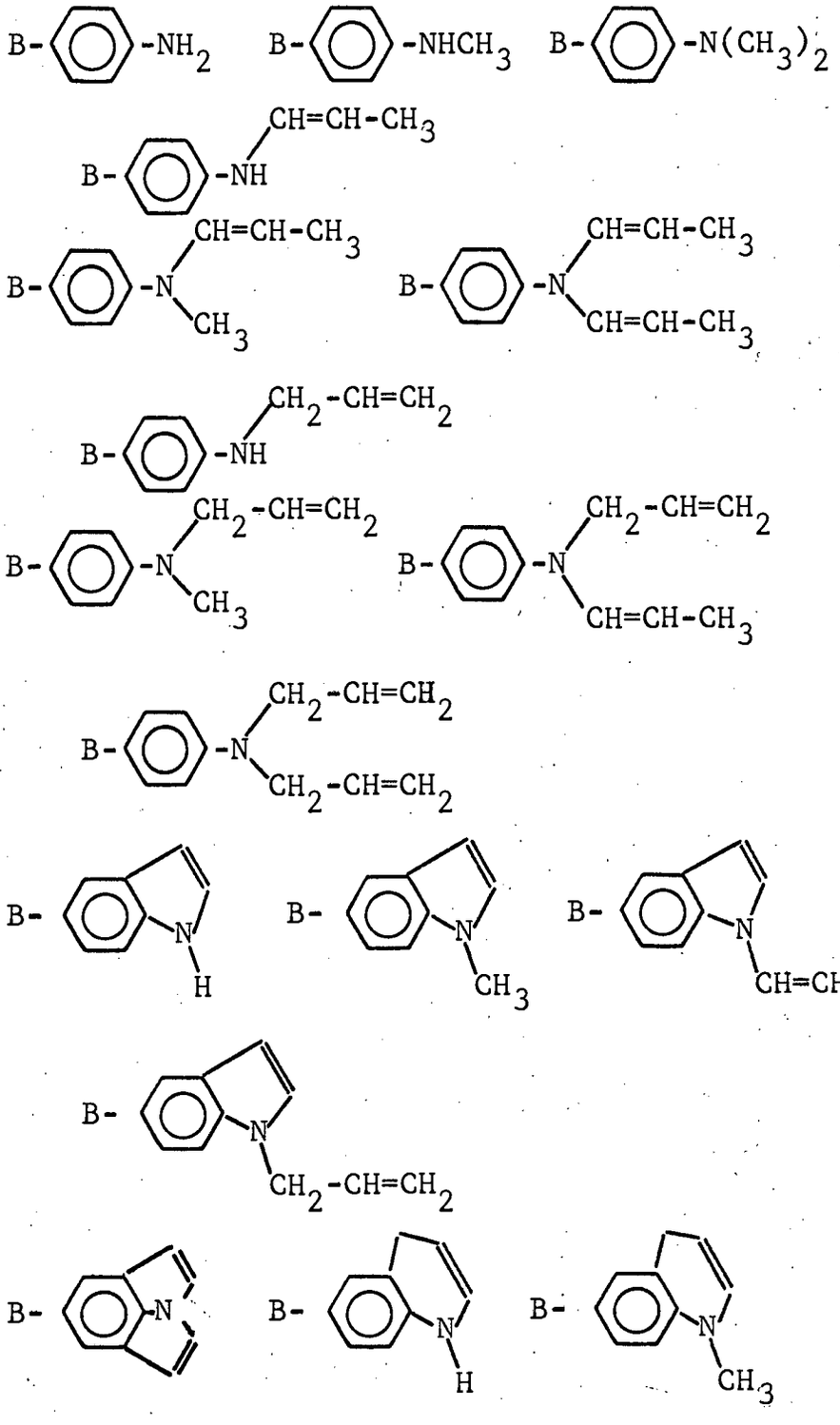


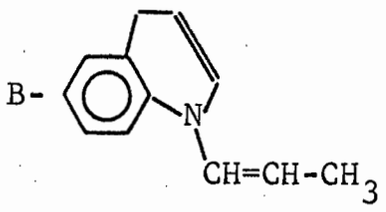
(iii) Diphenylmethane nucleus:

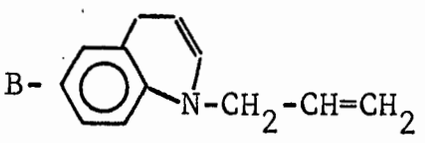
A denotes nitrogen containing function.

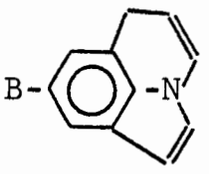


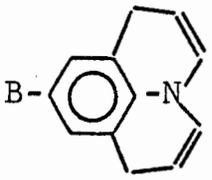
(iv) Nitrogen containing functions:











The total number of these possible condensible products is 369. In addition further products can be formed from structures in the resin containing aliphatic ether links formed by the elimination of water from two neighbouring hydroxyl groups (section F.7.c.).

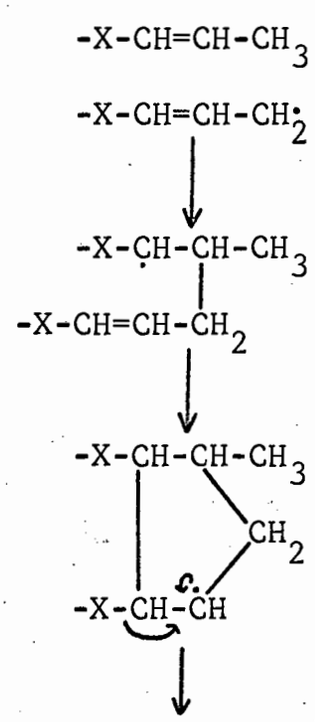
It is clear that the loss from the network of saturated degradation products must lead to the formation in the resin of a highly unsaturated structure. The term unsaturated implies the presence both of double bonds and of unpaired electrons. It is also evident that, because of this, the structure of the resin remaining in the latter stages of degradation bears little resemblence to the original structure. It was for this reason that the degradation was performed at as low a temperature and for as short a time as was consistent with the production of quantities of degradation products capable of isolation and analysis. The coloration of the resin bars which occurs during degradation is consistent with the highly unsaturated structure of the resin after degradation. It is probable that further cross-linking reactions involving both double bonds and radical recombination occur in the later stages of degradation. The extent of this cross-linking is not, however, such that the resin retains its original

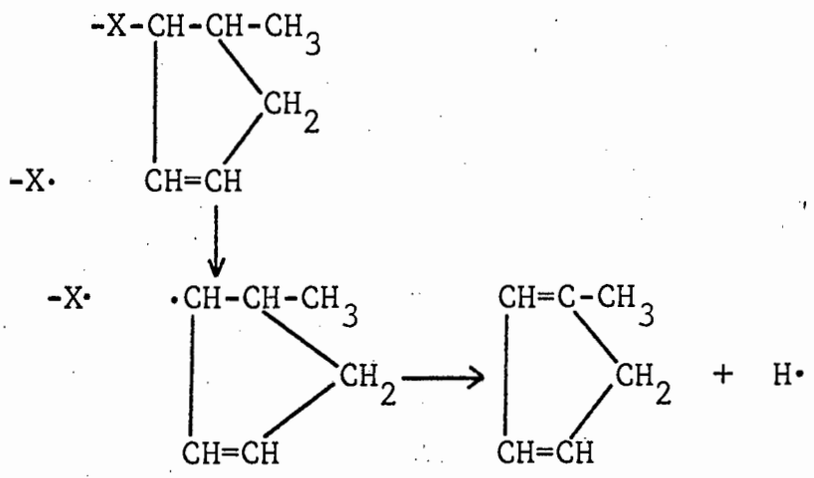
good mechanical (and electrical) properties. The resin bars after degradation were brittle, a property typically associated with rigid polymers of low molecular weight. The decrease in flexibility of the network which follows double bond formation in the network has been discussed (section F.3.)

Lee[35] reported the presence of methylcyclopentadiene as a product of the degradation at 450°C of this resin/hardener system. This substance is almost certainly formed from the structure which remains after dehydration reactions and reactions to form phenolic, basic and benzofuryl products. Because of the substantially lower temperatures used in this investigation methylcyclopentadiene was not produced in significant amounts. Methylcyclopentadiene may be formed in the following way:

(X denotes oxygen or nitrogen)

A propenyl radical attacks a propenyl 'free end'. Both are likely to be present in large quantities in the latter stages of degradation. Further reactions lead to the product:




-X-CH-CH-CH3
CH2
-X·
CH=CH
-X·
·CH-CH-CH3
CH2
CH=CH
CH=C-CH3
CH2
CH=CH
+ H·

F.8: Conclusion

The degradation of the adduct of the diglycidyl-ether of Bisphenol A and p,p'-diaminodiphenylmethane may be considered as occuring in four stages.

(i) The first stage involves scission of bonds in the network (most probably the aryl-methylene and aryl-isopropyl bonds) to form free radical ends. These recombine or occasionally may abstract hydrogen from neighbouring portions of the network to form saturated free ends or, in the latter case, may disproportionate to form phenyl and isopropenylphenyl free ends. Under isothermal conditions this stage appears between 220°C and 240°C.

(ii) At higher temperatures or as the temperature is raised a dehydration reaction changes the structure of the network and paves the way for its further degradation. Under isothermal conditions dehydration probably starts at temperatures above 250°C or thereabouts.

(iii) The dehydrated and weakened network breaks down to form phenolic, basic and benzofuryl structures together with many other minor products. This process becomes appreciable at temperatures above 290°C under isothermal conditions.

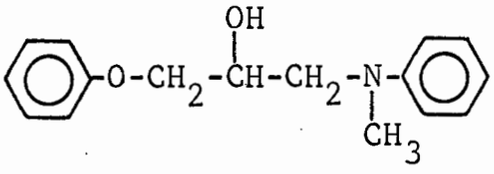
(iv) At higher temperatures the remaining structure which is highly unsaturated may break down to give further products (for example, methylcyclopentadiene).

The reaction mechanisms which have been formulated for the process are likely to be general for amine-cured epoxide resins. The precise nature of the products expected from the degradation of any particular resin/amine hardener system will depend on its chemical structure. It is clear that no amine-cured epoxide

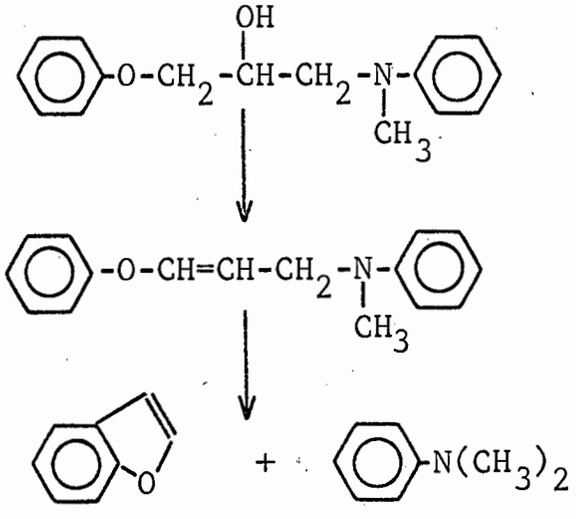
resin, whatever its structure, is likely to be a useful material at temperatures above 230°C.

G: Note on a possible Synthetic Method for Benzofurans

The formation of large quantities of products containing the benzofuran nucleus suggests a possible method for the synthesis of such compounds. For example the dry distillation of the adduct of phenylglycidylether and N-methylaniline:



may lead to the formation of benzofuran via the following reactions:



The alternative dehydration reaction may yield phenol and N-methyl-N-propenylaniline. Both the basic and acidic products are easily removed. Better yields would be expected if the intermediate dehydrated structure were used as the starting product.

H: Summary

The low temperature thermal degradation *in vacuo* of the adduct of the diglycidylether of Bisphenol A and *p,p'*-diaminodiphenylmethane was investigated. Measurements of the dielectric properties in the frequency range 210 c/s to 90 kc/s and in the temperature range -196°C to 240°C revealed the presence of two dispersion regions. The low temperature region was associated with movement of pendant hydroxyl groups. The high temperature region characterised the glass transition of the network. Degradation of the network caused a decrease of the absorption in the low temperature region and caused a shift of the glass transition to lower temperatures. These effects were discussed in relation to the changes in the chemical structure of the network which accompany its degradation. The major condensible products of the degradation at a temperature of 304°C were isolated and identified. These were water, Bisphenol A, 2-(benzofur-5-yl)-2-(*p*-hydroxyphenyl) propane, *N,N,N',N'*-tetramethyl-*p,p'*-diaminodiphenylmethane, phenol, *p*-isopropylphenol, *p*-isopropenylphenol, *N,N*-dimethylaniline, *N*-methylaniline, *N,N*-dimethyl-*p*-toluidine, *N*-methyl-*p*-toluidine and benzofuran. The presence of 2,2-bis-(benzofur-5-yl)propane was suspected. The gaseous degradation products were identified as acetaldehyde, chloromethane, carbon dioxide, carbon monoxide, methane, ethane, ethene and nitrogen. Detailed reaction mechanisms were proposed to account for the formation of the products identified. The nature of minor condensible degradation products was discussed. A novel synthesis of *p*-isopropenylphenol

and the synthesis of 2-(benzofur-5-yl)-2-(p-hydroxyphenyl)propane which had not been reported previously in the literature were described.

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APPENDIX A

E.1.2.b: Dielectric results in tabular form

Experiment I Frequency: 1.05 kc/s.			Experiment II Frequency: 90 kc/s.		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-178	0.10	1.27	-171	0.15	1.94
-157	0.15	1.29	-155	0.25	1.97
-137	0.25	1.30	-141	0.30	1.99
-123	0.30	1.31	-131	0.35	2.02
-105	0.35	1.33	-121	0.40	2.04
92½	0.45	1.33	-111	0.50	2.06
- 86	0.45	1.36	-100	0.55	2.09
- 76½	0.55	1.36	- 91	0.75	2.12
- 72	0.55	1.38	- 81	0.90	2.16
- 56½	0.65	1.40	- 70	1.00	2.19
- 47½	0.80	1.42	- 59	1.05	2.23
- 37½	0.95	1.44	- 52	1.15	2.24
- 32	1.05	1.45	- 49½	1.15	2.26
- 27½	1.10	1.46	- 46	1.20	2.26
- 25½	1.05	1.47	- 43	1.25	2.29
- 23½	1.10	1.47	- 39½	1.35	2.30
- 20	1.15	1.48	- 35½	1.40	2.33
- 17	1.15	1.49	- 31	1.45	2.34
- 15½	1.15	1.49	- 28½	1.50	2.36
- 9½	1.10	1.51	- 25	1.60	2.37
1½	0.90	1.50	- 21	1.65	2.39
7½	0.80	1.53	- 18½	1.70	2.41
25	0.55	1.57	- 14½	1.75	2.42
37½	0.35	1.59	- 10	1.85	2.45
58½	0.20	1.58	- 4½	1.95	2.47
67	0.10	1.67	6	2.10	2.53
88	0.15	1.63	12½	2.25	2.56
105	0.20	1.66	20	2.30	2.60
116	0.50	1.71	25	2.40	2.64
132	0.40	1.83	32	2.40	2.68
134	0.25	2.26	42½	2.30	2.74
135	0.10	2.28	65	1.85	2.85
135	0.50	1.89	83	1.35	2.94
141	0.10	2.32	97	0.95	3.00
149	0.15	2.46	118	0.40	3.10
160	0.35	2.54	132	0.30	3.21
			143	0.25	3.19
			152	0.20	3.22
			161	0.20	3.28
			162	0.25	3.25
			173	0.25	3.33
			178	0.35	3.48
			184	0.50	3.53
			194	0.85	3.63
			204	1.25	3.84
			217	1.80	4.21
			230	2.30	4.48
			245	3.15	4.47

Frequency: 46 kc/s.			Frequency: 22 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-169	0.20	1.95	-169	0.25	1.95
-154	0.25	1.97	-152	0.30	1.98
-141	0.35	2.00	-140	0.35	2.00
-130	0.45	2.02	-129	0.45	2.03
-119	0.50	2.05	-118	0.50	2.05
-110	0.60	2.07	-109	0.60	2.08
- 99	0.65	2.10	- 98	0.65	2.11
- 90	0.75	2.13	- 89	0.75	2.15
- 80	0.85	2.17	- 79	0.85	2.18
- 69	1.00	2.20	- 69	0.95	2.22
- 58	1.05	2.24	- 57	1.05	2.25
- 51	1.10	2.25	- 50½	1.10	2.26
- 49	1.15	2.28	- 48	1.15	2.29
- 45½	1.20	2.28	- 45½	1.15	2.29
- 42½	1.25	2.31	- 42	1.20	2.32
- 39	1.30	2.31	- 38½	1.30	2.33
- 35	1.35	2.34	- 34½	1.35	2.36
- 31	1.45	2.36	- 30½	1.55	2.37
- 28	1.45	2.38	- 27½	1.60	2.40
- 24½	1.55	2.39	- 24½	1.65	2.41
- 20½	1.60	2.41	- 20½	1.75	2.43
- 18½	1.65	2.43	- 18	1.75	2.45
- 14½	1.75	2.44	- 14	1.85	2.46
- 10	1.80	2.47	- 9½	1.85	2.49
- 4	1.90	2.49	- 3½	2.05	2.52
6	2.10	2.53	6	2.10	2.58
12½	2.15	2.58	12½	2.20	2.61
20	2.20	2.63	20	2.15	2.66
25	2.20	2.67	25	2.15	2.70
32	2.15	2.71	32	2.05	2.74
42½	2.05	2.77	42½	1.85	2.80
65	1.45	2.86	65	1.10	2.88
83	1.00	2.95	83	0.70	2.96
97	0.65	3.01	97	0.45	3.02
118	0.40	3.10	118	0.25	3.12
132	0.20	3.21	132	0.20	3.22
143	0.20	3.20	143	0.20	3.20
152	0.20	3.22	151	0.15	3.22
161	0.20	3.28	161	0.20	3.29
162	0.20	3.26	162	0.25	3.26
173	0.25	3.34	173	0.25	3.34
178	0.45	3.49	178	0.50	3.49
184	0.60	3.54	184	0.65	3.55
194	0.90	3.65	194	1.00	3.67
205	1.40	3.87	205	1.75	3.90
217	2.00	4.27	217	2.60	4.32
230	2.95	4.52	230	4.31	4.57
245	4.75	4.51	245	7.67	4.60

Frequency: 10.5 kc/s.			Frequency 4.8 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ϵ	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ϵ
-168	0.25	1.95	-167	0.25	1.96
-151	0.30	1.98	-150	0.35	1.99
-139	0.40	2.01	-138	0.40	2.01
-128	0.40	2.03	-127	0.45	2.04
-118	0.50	2.05	-117	0.50	2.06
-108	0.60	2.09	-107	0.60	2.10
- 97	0.65	2.12	- 97	0.70	2.13
- 89	0.80	2.16	- 88	0.80	2.16
- 79	0.85	2.19	- 78	0.85	2.20
- 68	1.00	2.23	- 67	1.00	2.24
- 57	1.05	2.27	- 56	1.15	2.28
- 50½	1.15	2.28	- 50	1.25	2.29
- 48	1.20	2.31	- 47½	1.25	2.32
- 45	1.25	2.31	- 45	1.30	2.32
- 41½	1.25	2.34	- 41½	1.35	2.36
- 38½	1.35	2.35	- 38	1.40	2.36
- 34	1.40	2.38	- 34	1.50	2.39
- 30	1.50	2.39	- 29½	1.60	2.41
- 27	1.55	2.42	- 27	1.60	2.44
- 24	1.65	2.43	- 24	1.75	2.45
- 20	1.70	2.45	- 20	1.80	2.48
- 18	1.70	2.47	- 18	1.75	2.49
- 14	1.85	2.48	- 14	1.90	2.51
- 9½	1.85	2.52	- 9½	1.90	2.54
- 3	2.00	2.54	- 2½	2.00	2.57
5½	2.00	2.60	5½	1.95	2.63
12½	2.05	2.64	12½	1.90	2.66
20	1.95	2.69	20	1.80	2.71
25	1.90	2.73	25	1.65	2.75
32	1.70	2.77	32	1.45	2.79
42½	1.45	2.82	42½	1.20	2.84
65	0.90	2.90	65	0.65	2.90
83	0.50	2.96	83	0.35	2.97
97	0.30	3.02	97	0.25	3.02
118	0.20	3.12	118	0.15	3.12
132	0.15	3.22	132	0.15	3.22
143	0.20	3.20	143	0.15	3.20
151	0.15	3.22	151	0.15	3.22
161	0.20	3.29	161	0.20	3.29
161	0.20	3.28	162	0.30	3.27
162	0.25	3.27	173	0.35	3.35
173	0.30	3.34	178	0.60	3.51
178	0.55	3.50	184	0.90	3.58
184	0.75	3.57	194	1.60	3.72
194	1.20	3.69	206	2.85	3.98
206	2.20	3.93	217	5.30	4.45
217	3.55	4.38	230	11.70	4.93
230	7.30	4.66	245	21.85	5.10
245	13.10	4.78	245	21.85	5.10

Frequency: 2.4 kc/s.			Frequency 1.05 kc/s.		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-166	0.25	1.96	-164	0.25	1.97
-149	0.30	1.99	-148	0.30	2.00
-137	0.35	2.02	-136	0.40	2.03
-126	0.45	2.05	-125	0.45	2.05
-117	0.50	2.07	-116	0.55	2.08
-107	0.60	2.11	-105	0.60	2.12
- 96	0.70	2.14	- 95	0.65	2.15
- 87	0.80	2.17	- 86	0.80	2.19
- 78	0.85	2.21	- 77	0.85	2.23
- 66	1.00	2.25	- 66	1.05	2.27
- 53	1.10	2.30	- 53	1.20	2.32
- 49½	1.15	2.31	- 49	1.25	2.33
- 47	1.25	2.34	- 46½	1.35	2.36
- 44½	1.25	2.34	- 44	1.40	2.36
- 41	1.30	2.37	- 40½	1.40	2.39
- 38	1.40	2.38	- 37½	1.55	2.40
- 33½	1.50	2.41	- 33	1.55	2.44
- 29½	1.70	2.43	- 29	1.70	2.46
- 26½	1.60	2.46	- 26½	1.75	2.48
- 23½	1.80	2.47	- 23½	1.80	2.50
- 19½	1.90	2.50	- 19	1.80	2.52
- 17½	1.90	2.51	- 17½	1.80	2.54
- 13½	1.95	2.53	- 13	1.85	2.56
- 9½	1.88	2.57	- 9	1.75	2.59
- 2	1.95	2.60	- 2	1.75	2.63
+ 5½	1.85	2.64	5	1.55	2.67
12½	1.80	2.69	12½	1.45	2.71
20	1.50	2.73	20	1.20	2.76
25	1.35	2.78	25	1.15	2.79
32	1.15	2.81	32½	0.95	2.82
43	0.95	2.85	43	0.75	2.86
65	0.45	2.91	65	0.35	2.91
83	0.25	2.97	83	0.20	2.98
97	0.20	3.03	97	0.15	3.03
118	0.10	3.13	118	0.10	3.13
132	0.10	3.23	132	0.15	3.23
143	0.15	3.20	143	0.15	3.21
151	0.15	3.22	151	0.15	3.22
161	0.20	3.29	161	0.25	3.30
161	0.25	3.29	161	0.25	3.29
162	0.30	3.27	162	0.40	3.27
173	0.40	3.35	173	0.50	3.36
178	0.75	3.52	178	1.05	3.54
184	1.15	3.59	184	1.70	3.62
194	2.15	3.74	194	3.15	3.79
207	4.00	4.04	207	5.70	4.15
217	7.85	4.57	217	12.40	4.79
230	19.85	5.10	230	32.70	5.67
245	54.30	5.77	245	69.25	7.96

Frequency: 445 c/s			Frequency: 210 c/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-162	0.30	1.97	-159	0.25	1.98
-147	0.40	2.01	-146	0.35	2.02
-135	0.40	2.03	-133	0.40	2.04
-125	0.55	2.06	-124	0.55	2.07
-115	0.60	2.09	-115	0.60	2.10
-104	0.60	2.12	-103	0.60	2.13
- 95	0.75	2.16	- 94	0.90	2.17
- 85	0.80	2.20	- 85	0.90	2.22
- 77	0.95	2.24	- 76	0.95	2.25
- 65	1.06	2.28	- 65	1.25	2.30
- 53	1.30	2.34	- 52	1.45	2.36
- 48½	1.40	2.35	- 48	1.55	2.36
- 46½	1.30	2.38	- 46	1.55	2.39
- 43½	1.45	2.38	- 43½	1.65	2.39
- 40½	1.55	2.41	- 40	1.65	2.43
- 37	1.60	2.42	- 36½	1.70	2.45
- 33	1.70	2.46	- 32½	1.60	2.48
- 29	1.75	2.48	- 28½	1.75	2.50
- 26	1.70	2.51	- 25	1.70	2.53
- 23	1.85	2.52	- 23	1.80	2.54
- 19	1.80	2.55	- 18½	1.75	2.58
- 17	1.75	2.57	- 16½	1.75	2.57
- 13	1.75	2.59	- 13	1.70	2.61
- 9	1.65	2.62	- 8½	1.60	2.64
- 1½	1.60	2.66	- 1	1.40	2.68
5	1.35	2.69	5	1.20	2.71
12½	1.20	2.73	12½	1.00	2.74
20	0.95	2.77	20	0.95	2.79
25	0.85	2.80	25	0.75	2.81
32½	0.70	2.83	32½	0.55	2.84
43	0.55	2.87	43	0.45	2.87
65	0.25	2.92	65	0.15	2.92
83	0.20	2.98	83	0.20	2.98
97	0.15	3.03	97	0.15	3.03
118	0.15	3.13	118	0.20	3.13
132	0.10	3.23	132	0.20	3.23
143	0.20	3.21	143	0.25	3.21
151	0.15	3.22	151	0.15	3.22
161	0.35	3.30	161	0.50	3.30
162	0.50	3.29	161	0.50	3.31
178	1.55	3.56	162	0.80	3.29
184	2.40	3.66	173	0.95	3.38
194	4.50	3.87	178	2.10	3.59
207	8.25	4.31	184	3.30	3.71
217	20.00*	5.16	194	5.85	3.95
230	> 36.35*	no balance	208	12.30	4.50
245	> 36.35	no balance	217	> 17.15	no balance
			230	> 17.15	no balance
			245	> 17.15	no balance

*At these temperatures the value of $\tan\delta$ exceeded the maximum value which could be measured at this frequency (viz. 36.35×10^{-2}) and the bridge could not therefore be balanced. The maximum value of $\tan\delta$ that the bridge could measure at 210 c/s was 17.15×10^{-2} and at 1.05 kc/s was 85.80×10^{-2}.

Experiment III

Frequency: 90 kc/s.			Frequency: 46 kc/s.		
Temperature (°C)	tan δ (X 10^{-2})	ε	Temperature (°C)	tan δ (X 10^{-2})	ε
-176	0.15	2.36	-176	0.20	2.36
-149	0.25	2.43	-149	0.35	2.44
-140	0.30	2.46	-140	0.45	2.47
-131	0.40	2.50	-130	0.50	2.50
-123	0.45	2.52	-123	0.55	2.53
-112	0.55	2.56	-111	0.65	2.57
-102	0.75	2.60	-102	0.75	2.61
- 90	0.90	2.66	- 90	0.90	2.68
- 78	1.05	2.72	- 78	1.05	2.74
- 67	1.20	2.78	- 66	1.20	2.80
- 56	1.30	2.83	- 55½	1.30	2.85
- 45½	1.45	2.90	- 45	1.45	2.92
- 36	1.65	2.97	- 35½	1.60	3.00
- 20½	2.00	3.10	- 20½	1.95	3.13
- 12½	2.10	3.14	- 12½	2.10	3.16
- 1½	2.40	3.23	- 1½	2.40	3.27
11	2.65	3.35	11½	2.55	3.39
21½	2.75	3.45	21½	2.65	3.49
31½	2.80	3.55	21½	2.65	3.60
40½	2.80	3.63	40½	2.55	3.68
55	2.70	3.82	55	2.25	3.86
77	2.10	4.02	77	1.60	4.05
98	1.25	4.16	98	0.95	4.17
111	0.90	4.21	111	0.60	4.21
134	0.35	4.18	134	0.30	4.19
156	0.25	4.30	156	0.20	4.31
175	0.30	4.41	175	0.30	4.42
188	0.60	4.45	188	0.80	4.47
198	1.20	4.51	198	1.25	4.54
216	1.70	4.57	216	1.80	4.60
231	2.05	4.66	231	2.55	4.69

Frequency: 22 kc/s			Frequency: 10.5 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-176	0.25	2.36	-176	0.25	2.37
-148	0.35	2.45	-148	0.35	2.46
-139	0.40	2.48	-139	0.40	2.49
-130	0.50	2.51	-130	0.50	2.52
-123	0.55	2.53	-122	0.55	2.55
-111	0.65	2.58	-111	0.65	2.59
-102	0.70	2.63	-101	0.80	2.64
- 89	0.85	2.69	- 89	0.90	2.70
- 79	1.00	2.75	- 79	1.00	2.77
- 65	1.15	2.82	- 65	1.20	2.84
- 55	1.30	2.87	- 54½	1.30	2.89
- 44½	1.55	2.95	- 44½	1.45	2.98
- 35½	1.75	3.03	- 35	1.65	3.05
- 20	2.00	3.16	- 20	2.00	3.19
- 12½	2.15	3.20	- 12	2.25	3.23
- 1½	2.35	3.30	- 1½	2.35	3.35
11½	2.50	3.44	12	2.45	3.49
21½	2.50	3.54	22	2.35	3.59
32	2.45	3.64	32	2.20	3.68
40½	2.30	3.72	40½	1.90	3.76
55	1.35	3.94	55	1.35	3.94
77	1.15	4.07	77	0.90	4.10
98	0.60	4.19	98	0.40	4.20
112	0.40	4.22	112	0.30	4.23
134	0.20	4.19	135	0.20	4.20
156	0.20	4.31	156	0.15	4.31
175	0.35	4.42	175	0.35	4.43
188	0.80	4.48	188	1.00	4.50
198	1.45	4.57	198	1.70	4.59
216	2.20	4.64	216	2.90	4.69
231	3.90	4.73	232	6.45	4.80

Frequency: 4.8 kc/s			Frequency: 2.4 kc/s		
Temperature (°C)	tan δ (X 10^{-2})	ε	Temperature (°C)	tan δ (X 10^{-2})	ε
-176	0.20	2.37	-176	0.20	2.37
-147	0.40	2.46	-147	0.40	2.47
-138	0.45	2.50	-138	0.45	2.50
-129	0.55	2.53	-129	0.50	2.54
-122	0.60	2.56	-121	0.60	2.57
-110	0.65	2.60	-109	0.70	2.61
-101	0.75	2.65	-101	0.80	2.67
- 89	0.90	2.72	- 88	0.90	2.73
- 79	1.10	2.79	- 79	1.05	2.80
- 65	1.30	2.86	- 64	1.20	2.88
- 54½	1.35	2.91	- 53½	1.35	2.94
- 43½	1.55	3.00	- 43½	1.75	3.03
- 34½	1.70	3.08	- 34½	1.90	3.11
- 19½	2.00	3.22	- 19	2.15	3.25
- 12	2.15	3.27	- 11½	2.30	3.30
- 1	2.25	3.39	- ½	2.25	3.43
12	2.15	3.53	12½	2.10	3.57
22	2.05	3.63	22½	1.90	3.66
32½	1.80	3.72	32½	1.50	3.74
40½	1.60	3.79	40½	1.30	3.81
55	1.15	3.96	55	0.90	3.98
77	0.65	4.11	77	0.50	4.12
99	0.35	4.21	99	0.25	4.21
112	0.25	4.24	112	0.20	4.24
135	0.15	4.20	135	0.10	4.21
156	0.15	4.31	156	0.15	4.31
175	0.40	4.43	175	0.45	4.44
188	1.20	4.52	188	1.50	4.55
198	2.15	4.63	198	3.00	4.68
216	4.30	4.74	216	6.50	4.82
232	11.90	4.93	232	20.40	5.23

Frequency: 1.05 kc/s			Frequency: 445 c/s		
Temperature (°C)	tan δ (X 10^{-2})	ε	Temperature (°C)	tan δ (X 10^{-2})	ε
-176	0.25	2.37	-176	0.25	2.38
-147	0.40	2.48	-146	0.45	2.49
-137	0.50	2.52	-137	0.50	2.53
-129	0.55	2.55	-128	0.55	2.56
-121	0.60	2.58	-120	0.65	2.60
-109	0.75	2.63	-108	0.75	2.64
-101	0.85	2.68	-100	0.85	2.70
- 88	1.00	2.75	- 88	1.05	2.77
- 78	0.75	2.83	- 78	1.20	2.85
- 64	1.30	2.91	- 63	1.45	2.93
- 53½	1.45	2.97	- 53	1.55	2.99
- 42½	1.70	3.05	- 42½	1.75	3.09
- 34	1.85	3.14	- 33½	1.85	3.18
- 19	2.05	3.29	- 19	2.00	3.34
- 11½	2.25	3.34	- 11	2.00	3.39
- ½	2.05	3.48	- ½	1.75	3.51
12½	1.75	3.61	13	1.55	3.64
22½	1.55	3.69	23	1.25	3.72
32½	1.25	3.77	32½	0.95	3.79
40½	1.05	3.84	40½	0.80	3.86
55	0.70	4.00	55	0.55	4.01
77	0.40	4.12	77	0.35	4.13
99	0.20	4.21	99	0.20	4.21
112	0.15	4.24	112	0.15	4.24
135	0.10	4.12	135	0.10	4.21
156	0.15	4.31	156	0.15	4.32
175	0.60	4.45	175	0.95	4.46
188	2.20	4.58	188	3.45	4.64
198	4.35	4.75	198	6.60	4.86
216	10.25	4.98	216	16.50	5.29
234	37.60	6.02	234	36.35	no balance

Experiment IV

Frequency: 210 c/s			Frequency: 90 kc/s		
Temperature (°C)	$\tan\delta_2$ ($\times 10^{-2}$)	ϵ	Temperature (°C)	$\tan\delta_2$ ($\times 10^{-2}$)	ϵ
-176	0.20	2.38	-184	0.15	2.26
-146	0.45	2.50	-176	0.15	2.28
-136	0.50	2.53	-164	0.25	2.31
-128	0.65	2.57	-149	0.30	2.35
-170	0.65	2.61	-139	0.35	2.38
-108	0.70	2.65	-129	0.40	2.41
-100	0.95	2.71	-117	0.50	2.45
- 88	1.05	2.79	-105	0.60	2.50
- 77	1.25	2.87	- 92	0.85	2.55
- 63	1.40	2.96	- 79	1.00	2.61
- 52½	1.55	3.02	- 67	1.15	2.67
- 42	1.75	3.12	- 54½	1.30	2.73
- 33½	2.00	3.21	- 44	1.50	2.80
- 18½	2.00	3.37	- 32½	1.70	2.88
- 11	1.90	3.43	- 24	1.90	2.95
- ½	1.65	3.55	- 11½	2.10	3.05
13	1.25	3.67	- 2½	2.30	3.13
23	1.05	3.74	7	2.70	3.27
32½	0.75	3.81	19½	2.75	3.35
40½	0.65	3.87	30	2.50	3.55
55	0.45	4.02	43½	2.50	3.76
77	0.25	4.14	64	2.55	4.05
99	0.15	4.22	74	2.20	4.09
112	0.15	4.25	95	1.40	4.26
135	0.15	4.21	123	0.50	4.29
156	0.25	4.32	132	0.40	4.24
175	1.25	4.48	149	0.30	4.27
188	4.95	4.70	165	0.25	4.31
198	9.30	5.02	181	0.50	4.42
216	> 17.15	no balance	194	1.15	4.49
234	> 17.15	no balance	207	1.70	4.52
			222	1.95	4.53
			236	2.40	4.52

Frequency: 46 kc/s			Frequency: 22 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-184	0.15	2.26	-184	0.15	2.26
-175	0.20	2.29	-174	0.25	2.29
-162	0.25	2.31	-161	0.30	2.32
-148	0.35	2.36	-147	0.35	2.36
-138	0.45	2.38	-137	0.40	2.39
-128	0.50	2.42	-127	0.45	2.43
-116	0.60	2.46	-116	0.55	2.47
-103	0.70	2.51	-103	0.65	2.52
- 91	0.85	2.56	- 91	0.75	2.58
- 79	1.00	2.63	- 78	0.90	2.64
- 66	1.10	2.69	- 65	1.05	2.70
- 53½	1.30	2.75	- 53½	1.20	2.77
- 43½	1.45	2.82	- 43	1.35	2.84
- 32	1.65	2.91	- 32	1.70	2.94
- 23½	1.80	2.98	- 23½	1.90	3.01
- 11½	2.10	3.08	- 11	2.10	3.12
- 2½	2.25	3.17	- 2	2.25	3.20
7	2.70	3.30	7	2.50	3.34
19½	2.60	3.39	19½	2.40	3.44
30	2.90	3.60	30	2.55	3.65
43½	2.75	3.81	43½	2.30	3.86
64	2.10	4.09	64	1.65	4.12
74	1.70	4.12	74	1.30	4.15
95	1.00	4.27	95	0.65	4.29
123	0.45	4.30	123	0.30	4.31
132	0.30	4.25	132	0.30	4.26
149	0.25	4.27	149	0.25	4.27
165	0.25	4.32	165	0.25	4.32
181	0.60	4.44	181	0.65	4.45
194	1.30	4.51	194	1.60	4.54
208	1.90	4.56	208	2.40	4.59
222	2.25	4.56	223	3.50	4.59
234	3.40	4.55	233	5.50	4.58

Frequency: 10.5 kc/s			Frequency: 4.8 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-184	0.15	2.27	-184	0.20	2.27
-168	0.25	2.31	-168	0.25	2.31
-158	0.30	2.34	-157	0.30	2.35
-144	0.35	2.38	-143	0.40	2.39
-133	0.45	2.42	-132	0.45	2.43
-124	0.55	2.45	-124	0.55	2.46
-113	0.65	2.50	-113	0.65	2.51
-101	0.75	2.56	-101	0.80	2.57
- 90	0.85	2.61	- 89	0.95	2.63
- 77	1.00	2.69	- 77	1.05	2.70
- 64	1.20	2.75	- 64	1.25	2.78
- 52½	1.35	2.83	- 52	1.45	2.85
- 42	1.65	2.91	- 42	1.65	2.94
- 31	1.90	3.02	- 30½	1.90	3.05
- 23	2.05	3.10	- 22½	2.00	3.14
- 10	2.20	3.22	- 9½	2.05	3.26
- ½	2.20	3.32	0	1.95	3.36
7	2.40	3.48	7	2.00	3.53
19½	1.95	3.56	19½	1.55	3.59
30	1.80	3.77	30	1.35	3.80
43½	1.30	3.96	43½	1.05	3.99
64	0.75	4.19	64	0.55	4.20
73	0.55	4.19	73	0.40	4.20
95	0.30	4.31	95	0.25	4.32
123	0.20	4.32	123	0.20	4.32
132	0.15	4.27	132	0.15	4.27
149	0.20	4.29	149	0.25	4.29
165	0.35	4.34	165	0.50	4.35
181	1.35	4.50	181	2.25	4.52
194	4.00	4.64	194	6.85	4.70
208	9.80	4.75	208	20.40	4.94
223	20.40	4.87	223	42.60	5.66
234	48.0	5.68	234	>85.8	no balance

Frequency: 2.4 kc/s			Frequency: 1.05 kc/s		
Temperature (°C)	$\tan_{-2}$ (X 10^{-2})		Temperature (°C)	$\tan_{-2}$ (X 10^{-2})	
-184	0.15	2.27	-184	0.20	2.27
-168	0.25	2.31	-168	0.25	2.31
-158	0.30	2.34	-157	0.30	2.35
-144	0.35	2.38	-143	0.40	2.39
-133	0.45	2.42	-132	0.45	2.43
-124	0.55	2.45	-124	0.55	2.46
-113	0.65	2.50	-113	0.65	2.51
-101	0.75	2.56	-101	0.80	2.57
- 90	0.85	2.61	- 89	0.95	2.63
- 77	1.00	2.69	- 77	1.05	2.70
- 64	1.20	2.75	- 64	1.25	2.78
- 52½	1.35	2.83	- 52	1.45	2.85
- 42	1.65	2.91	- 42	1.65	2.94
- 31	1.90	3.02	- 30½	1.90	3.05
- 23	2.05	3.10	- 22½	2.00	3.14
- 10	2.20	3.22	- 9½	2.05	3.26
- ½	2.20	3.32	0	1.95	3.36
7	2.40	3.48	7	2.00	3.53
19½	1.95	3.56	19½	1.55	3.59
30	1.80	3.77	30	1.35	3.80
43½	1.30	3.96	43½	1.05	3.99
64	0.75	4.19	64	0.55	4.20
73	0.55	4.19	73	0.40	4.20
95	0.30	4.31	95	0.25	4.32
123	0.20	4.32	123	0.20	4.32
132	0.15	4.27	132	0.15	4.27
149	0.20	4.29	149	0.25	4.29
165	0.35	4.34	165	0.50	4.35
181	1.35	4.50	181	2.25	4.52
194	4.00	4.64	194	6.85	4.70
208	9.80	4.75	208	20.40	4.94
223	20.40	4.87	223	42.60	5.66
234	48.0	5.68	234	> 85.8	no balance

Frequency: 445 c/s			Frequency: 210 c/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ϵ	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ϵ
-184	0.10	2.28	-184	0.15	2.28
-167	0.25	2.32	-166	0.15	2.33
-156	0.30	2.36	-152	0.20	2.37
9142	0.45	2.40	-141	0.40	2.41
-132	0.50	2.43	-131	0.60	2.44
-123	0.60	2.47	-122	0.90	2.48
-112	0.70	2.53	-111	0.90	2.53
-100	0.75	2.58	- 99	0.95	2.59
- 88	0.90	2.65	- 87	1.05	2.67
- 76	1.15	2.72	- 76	1.20	2.74
- 63	1.30	2.80	- 62	1.30	2.84
- 51½	1.50	2.88	- 51	1.60	2.91
- 41½	1.70	2.98	- 41	1.90	3.00
- 30½	1.90	3.09	- 30	1.85	3.12
- 22½	2.10	3.18	- 22	2.00	3.20
- 9½	1.90	3.30	- 9	1.75	3.34
1	1.75	3.41	1½	1.45	3.44
7	1.70	3.56	7	1.50	3.60
19½	1.30	3.62	19½	1.05	3.64
30	1.05	3.82	30	0.80	3.83
43½	0.80	4.01	43½	0.60	4.02
65	0.50	4.23	65	0.45	4.23
73	0.35	4.21	73	0.35	4.22
95	0.20	4.32	95	0.20	4.32
123	0.20	4.32	124	0.20	4.33
132	0.20	4.27	132	0.25	4.27
149	0.35	4.29	149	0.50	4.30
165	0.90	4.36	165	1.80	4.36
181	4.25	4.56	181	7.60	4.60
194	6.85	4.70	195	> 17.15	no balance
208	> 36.35	no balance	195	> 17.15	no balance
223	> 36.35	no balance	223	> 17.15	no balance
234	> 36.35	no balance	234	> 17.15	no balance

Experiment V

Frequency: 90 kc/s			Frequency: 46 kc/s		
Temperature (°C)	tan δ (X 10^{-2})	ε	Temperature (°C)	tan δ (X 10^{-2})	ε
-168	0.10	1.81	-168	0.15	1.81
-158	0.15	1.83	-157	0.20	1.83
-147	0.20	1.84	-146	0.20	1.85
-134	0.25	1.86	-134	0.25	1.86
-124	0.30	1.88	-123	0.30	1.88
-112	0.35	1.90	-111	0.40	1.91
-102	0.40	1.92	-101	0.50	1.93
- 92	0.45	1.95	- 91	0.55	1.95
- 81	0.55	1.97	- 80	0.65	1.98
- 70	0.70	2.00	- 69	0.70	2.01
- 56	0.80	2.03	- 56	0.80	2.04
- 45½	0.90	2.06	- 45	0.95	2.07
- 37	1.00	2.09	- 36½	1.05	2.10
- 28½	1.10	2.12	- 28½	1.15	2.13
- 17	1.25	2.16	- 16½	1.30	2.18
- 6½	1.45	2.21	- 6	1.40	2.22
+ 5	1.55	2.25	5	1.50	2.27
20½	1.70	2.34	20½	1.55	2.36
37	1.55	2.46	37	1.35	2.47
46	1.45	2.52	46	1.15	2.54
63	1.10	2.68	63	0.90	2.69
78	0.90	2.80	78	0.65	2.81
94	0.55	3.09	94	0.50	3.09
111	0.50	3.19	111	0.50	3.20
127	0.85	3.41	127	0.80	3.42
134	1.05	3.52	134	1.10	3.54
145	1.80	3.70	145	1.90	3.72
161	3.00	3.68	161	3.35	3.73
182	4.00	3.83	182	4.65	3.89
194	5.10	3.90	194	6.90	3.97
206	6.90	3.95	206	9.75	4.04
226	12.00	4.09	226	19.90	4.28
236	17.90	4.24	236	30.50	4.64

Frequency: 22 kc/s			Frequency: 10.5 kc/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-168	0.15	1.82	-168	0.15	1.82
-156	0.20	1.83	-156	0.20	1.84
-144	0.25	1.85	-143	0.25	1.85
-133	0.25	1.87	-132	0.25	1.87
-122	0.35	1.89	-121	0.30	1.89
-110	0.35	1.91	-109	0.40	1.92
-100	0.45	1.93	- 99	0.45	1.94
- 91	0.50	1.96	- 90	0.50	1.97
- 79	0.55	1.98	- 79	0.55	2.00
- 68	0.65	2.02	- 67	0.65	2.03
- 55½	0.75	2.05	- 55	0.80	2.06
- 44½	0.80	2.08	- 44½	0.90	2.09
- 36½	0.95	2.11	- 36	1.00	2.12
- 28	1.10	2.15	- 27½	1.20	2.16
- 16	1.25	2.19	- 15½	1.30	2.21
- 5½	1.35	2.24	- 5	1.40	2.25
+ 5½	1.50	2.29	+ 6	1.35	2.31
20½	1.35	2.37	20½	1.10	2.39
37	1.00	2.49	37	0.85	2.50
46	0.85	2.55	46	0.70	2.56
63	0.60	2.70	63	0.45	2.71
78	0.50	2.81	78	0.35	2.82
94	0.35	3.10	94	0.30	3.11
111	0.40	3.21	111	0.35	3.22
127	0.75	3.44	127	0.80	3.45
134	1.05	3.56	134	1.20	3.58
145	2.10	3.76	145	2.45	3.80
161	3.60	3.79	161	4.15	3.85
182	5.55	3.96	181	7.90	4.05
194	10.30	4.08	194	18.40	4.28
206	16.80	3.20	206	30.00	4.63
226	36.50	4.88	226	64.40	6.85
236	58.90	5.96	236	94.40	10.03

Frequency: 4.8 kc/s			Frequency: 2.4 kc/s		
Temperature (°C)	$\tan\delta_2$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta_2$ ($\times 10^{-2}$)	ε
-167	0.15	1.82	-166	0.15	1.83
-154	0.20	1.84	-152	0.20	1.84
-141	0.25	1.86	-141	0.25	1.86
-131	0.25	1.88	-130	0.30	1.88
-119	0.35	1.90	-118	0.35	1.90
-109	0.40	1.92	-108	0.40	1.93
- 98	0.45	1.95	- 97	0.45	1.95
- 90	0.45	1.97	- 89	0.50	1.98
- 78	0.55	2.00	- 78	0.65	2.01
- 67	0.65	2.04	- 66	0.75	2.04
- 54½	0.80	2.06	- 53½	0.85	2.08
- 44	0.95	2.10	- 44	1.05	2.11
- 36	1.15	2.13	- 35½	1.20	2.15
- 27½	1.30	2.17	- 27	1.35	2.19
- 15	1.35	2.23	- 15	1.40	2.25
- 5	1.35	2.28	- 4	1.30	2.29
+ 6	1.20	2.32	+ 6	1.05	2.34
20½	0.90	2.40	20½	0.75	2.41
37	0.60	2.51	37	0.50	2.52
46	0.55	2.57	46	0.40	2.57
63	0.40	2.71	63	0.30	2.71
78	0.30	2.83	78	0.25	2.83
94	0.25	3.11	94	0.25	3.11
111	0.35	3.22	111	0.35	3.23
127	0.90	3.47	127	1.05	3.49
134	1.45	3.61	134	1.75	3.64
145	2.80	3.85	146	3.45	3.90
162	5.30	3.94	162	7.10	4.03
181	12.00	4.17	181	20.15	4.37
194	32.50	4.81	194	55.80	6.11
206	50.90	5.83	206	77.60	8.51
226	94.10	11.46	226	116.00	19.34
236	130.0	19.17	236	103.20	20.93

Frequency: 1.05 kc/s			Frequency: 445 c/s		
Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε	Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-166	0.15	1.83	-165	0.20	1.83
-151	0.20	1.85	-149	0.25	1.85
-140	0.25	1.87	-138	0.30	1.87
-130	0.30	1.89	-129	0.40	1.89
-117	0.40	1.91	-117	0.40	1.91
-107	0.40	1.94	-106	0.50	1.94
- 97	0.45	1.96	- 96	0.50	1.97
- 89	0.55	1.99	- 88	0.50	2.00
- 77	0.65	2.02	- 77	0.65	2.03
- 66	0.85	2.05	- 65	0.95	2.06
- 53½	1.00	2.09	- 53	1.10	2.10
- 42½	1.25	2.13	- 42½	1.40	2.15
- 35	1.35	2.16	- 35	1.45	2.18
- 27	1.40	2.21	- 26½	1.45	2.20
- 14½	1.35	2.27	- 14	1.20	2.29
- 3½	1.20	3.30	- 3	1.00	2.33
+ 7	0.85	2.35	+ 7½	0.60	2.36
20½	0.60	2.42	26½	0.40	2.43
37	0.40	2.52	37	0.40	2.53
46	0.35	2.58	46	0.35	2.58
63	0.25	2.72	63	0.20	2.72
78	0.25	2.84	78	0.20	2.84
94	0.20	3.12	94	0.20	3.12
111	0.40	3.24	111	0.50	3.24
127	1.30	3.52	127	1.70	3.54
134	2.05	3.67	134	2.65	3.72
146	4.40	3.98	146	5.80	4.09
162	11.00	4.16	162	19.15	4.41
180	35.95	5.02	180	>36.35	no balance
194	76.20	9.33	194	>36.35	no balance
206	>85.80	no balance	206	>36.35	no balance
226	>85.80	no balance	226	>36.35	no balance
236	>85.80	no balance	236	>36.35	no balance

Frequency: 210 c/s

Temperature (°C)	$\tan\delta$ ($\times 10^{-2}$)	ε
-164	0.15	1.84
-148	0.25	1.86
-137	0.45	1.87
-127	0.45	1.90
-116	0.60	1.91
-105	0.65	1.94
- 95	0.70	1.98
- 86	0.85	2.00
- 76	1.00	2.04
- 64	1.10	2.08
- 52½	1.30	2.11
- 42	1.75	2.16
- 34½	1.40	2.20
- 26	1.15	2.24
- 13½	0.85	2.30
- 1½	0.85	2.33
+ 8	0.40	2.38
20½	0.30	2.43
37	0.30	2.54
46	0.25	2.59
63	0.15	2.73
78	0.25	2.85
94	0.20	3.13
111	0.45	3.25
127	2.00	3.58
134	3.30	3.77
146	7.90	4.20
162	>17.15	no balance
180	>17.15	no balance
194	>17.15	no balance
206	>17.15	no balance
226	>17.15	no balance
236	>17.15	no balance

APPENDIX B: Infra-red spectra

1. The cured resin
2. The degraded resin
3. Benzofuran
4. 2-(Benzofur-5-yl)-2-(p-hydroxyphenyl)propane
5. 2,2-Bis-(benzofur-5-yl)propane
6. Bisphenol A
7. Bisphenol A 2,2-diethoxyethyl ether
8. p,p'-Diaminodiphenylmethane
9. Diglycidylether of Bisphenol A
10. 2-(p-Hydroxyphenyl)propan-2-ol
11. p-Isopropenylphenol
12. p-Isopropenylphenyl benzoate
13. p-Isopropylphenol
14. p-Isopropylphenyl benzoate
15. N,N,N',N'-Tetramethyl-p,p'-diaminodiphenylmethane
16. Gaseous products of degradation